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PROCEEDINGS

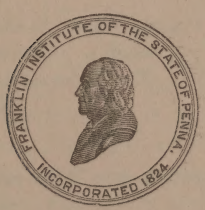
OF THE

CHEMICAL SECTION

OF THE

FRANKLIN INSTITUTE.

(VOL. I.—JAN.–DEC., 1889.)



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PROCEEDINGS

OF THE

CHEMICAL SECTION,

OF THE

FRANKLIN INSTITUTE.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, December 18, 1888.*]

HALL OF THE FRANKLIN INSTITUTE.

PHILADELPHIA, December 18, 1888.

Mr. J. H. EASTWICK, President, in the Chair.

Members present: Dr. L. B. Hall, Dr. S. C. Hooker, Dr. H. W. Jayne, Messrs. Luthy, Macfarlane, Chase, Bower, Pemberton, Matos and Palmer.

The bills for printing were approved, and ordered to be paid.

Mr. John G. Bullock's resignation as a member of the Section was accepted.

Mr. Philip E. Clarkson, of Quaker City Dye Works, and Mr. Jacob Lichenheim, 1614 North Tenth Street, Philadelphia, were elected full members of the Section.

The following gentlemen were nominated for membership in the Section: Mr. F. C. Lewin, 1011 Spruce Street, Philadelphia; Mr. C. V. Petraeus, 231 South Front Street, Philadelphia; Mr. R. E. Fisher, 2239 St. Alban's Place, Philadelphia; Dr. Wm. H. Greene, 204 North Thirty-sixth Street, Philadelphia; Dr. Geo. A. Koenig, University of Pennsylvania, Philadelphia; Mr. Henry C. Lea, 2000 Walnut Street, Philadelphia; Prof. Henry Morton, Stevens Institute, Hoboken, N. J.

The following gentlemen were elected officers of the Section for the year 1889:

President, Mr. H. Pemberton, Jr.
Vice Presidents, Dr. S. C. Hooker, Mr. T. C. Palmer.
Secretary, Dr. Wm. C. Day.
Treasurer, Dr. H. W. Jayne.
Conservator, Dr. Wm. H. Wahl.

Mr. H. Pemberton, Jr., presented a communication from Dr. Wm. H. Wahl, Secretary of the INSTITUTE, concerning the publishing of papers read before the Section, in the JOURNAL OF THE INSTITUTE, simultaneously with other journals to be selected by the Section.

The President appointed as a committee to confer with Dr. Wahl on this matter, Mr. H. Pemberton, Jr., Dr. S. C. Hooker.

The following were appointed a committee to revise the membership list, and re-arrange the By-Laws of the Section: Mr. T. C. Palmer, Dr. H. W. Jayne, Mr. R. L. Chase.

Mr. O. Luthy exhibited a piece of the mineral eudialyte, from Greenland. This species is a prominent source of zirconium. Mr. Luthy stated that it had lately been found in large quantities in the above country, near the cryolite locality. Twenty tons had been shipped to Europe at one time. Dr. Jayne stated that this material is largely imported into this country from Sweden, being used in the manufacture of the films for the Welsbach gas lights.

Mr. Chase remarked that there has been much difficulty in getting a film for these lamps that will be durable. Cases have been known where these films were broken by the slight jar caused on a floor above by falling boxes.

Dr. Hooker remarked that the burette, exhibited by him in October, was thought at the time to be new. He had since had his attention called to the figure of a burette almost identical with this.

Dr. Hooker showed several samples of sugar said to have been refined by the aid of electricity. These samples are different in appearance from any sugars heretofore in the market, but Dr. Hooker was of the opinion that much nonsense had been published by the non-scientific press on the subject of sugar-making by electricity; that it would be very easy to give granulated sugar this same appearance by caking and passing through a sieve. Mr. Luthy had also investigated the matter, and had concluded that this so-called electrically-refined sugar is only ordinary sugar specially prepared.

Mr. Macfarlane showed a copy of the souvenir published by Meister, Lucius & Bruening, on their twenty-fifth anniversary, July 2, 1888. This souvenir contains statistics of the growth and present dimensions of the great color works of this house, bird's-eye views of the buildings, maps of the enclosures, etc.; also a very beautiful spectrum of colors (all artificial) dyed on yarn.

Dr. Hooker showed a sample of saccharine, and remarked that many tests had been proposed for its detection, but that the most reliable one was based on the following principle:

The suspected substance is treated with ether, the extract evaporated and the residue fused with caustic potash, when if saccharine is present, salicylic acid is formed, and may be detected by the violet color formed with ferric chloride.

Dr. Jayne mentioned the fact that the use of saccharine had been prohibited in France for certain purposes, for revenue reasons. The same is true in England. Dr. Hooker stated that the evidence seemed to show that saccharine impairs the digestive process. Dr. Hall thought that this was doubtful, German authorities of high rank altogether dissenting.

Adjourned. T. C. PALMER, *Secretary.*

On the Detection of Fahlberg's Saccharine.

By Samuel C. Hooker, Ph. D.

[*To be read January 15, 1889.*]

A test has been recently described by E. Börnstein * for the detection of saccharine, based upon the supposed formation of a sulpho-phtaleïn. Saccharine is heated with a slight excess of resorcine and a few drops of concentrated sulphuric acid; on the addition of water a solution is obtained which fluoresces strongly when rendered alkaline.

I wish to point out that this test is rendered valueless by an observation I made about a year ago. Resorcine, when treated with sulphuric acid *alone*, gives apparently precisely the same reaction as that which Börnstein describes as characteristic of saccharine.

The reaction has unfortunately been already used in several instances which have come under my notice, and the presence of saccharine inferred in cases in which it was probably altogether absent.

It has long been known that resorcine, when heated with zinc chloride, also gives rise to products which fluoresce strongly.

A Rapid Colorimetric Method for the Estimation of Nitrates in Natural Waters.

By Samuel C. Hooker, Ph. D.

[*Read October 21, 1888.*]

It was long ago observed by Graebe and Glaser,* that the addition of oxidizing agents, in small quantity, to carbazol dissolved in concentrated sulphuric acid, gave rise to an intensely green solution. Up to the present time no useful application has been made of this reaction.

* *Berichte*, **21**, 488, R.

In devising a process for the rapid estimation of nitrates in the minute quantities in which they occur in natural waters, I have taken advantage of this property of carbazol. I have ascertained that under certain conditions, water containing as little as two parts of nitric acid per million gives a distinct reaction with the sulphuric-acid solution of carbazol; and that within certain limits the intensity of the color produced may be taken as the measure of the nitric acid present.

The estimation briefly described, omitting the necessary precautions, is conducted as follows: A measured quantity of the water, 2 cc. or less according to circumstances, is mixed with about 4 cc. of concentrated sulphuric acid, and when this has cooled a small quantity of sulphuric acid containing carbazol in solution is added. The green color produced is compared with that given by standard solutions of potassic nitrate, under precisely similar conditions, until the color is closely matched. The estimation is very rapidly effected, and provided the water contains as much nitric acid as two parts per million, as is very often the case, it need not be concentrated by evaporation.

The details of this process, together with the precautions to be taken in the presence of chlorides, nitrites, etc., will be described shortly in a paper giving the results of analyses made with the object of testing the delicacy of the method.

In conclusion, I would suggest the possibility that other compounds, diphenylamine or brucine, for instance, may prove as serviceable as carbazol for the purpose here described.

---

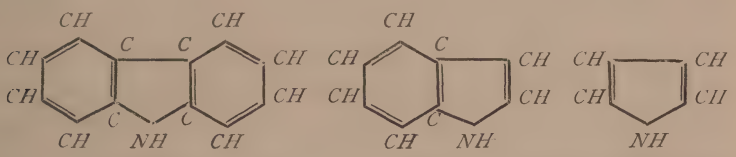
* *Ann.*, **163**, 347.

ON THE RELATIONS EXISTING BETWEEN CARBAZOL AND PYRROL.

BY SAMUEL C. HOOKER, Ph. D.

[*To be read January 15, 1889.*]

The theoretical relation existing between carbazol, indol and pyrrol is well shown by comparing their formulæ as follows:



The analogy existing between indol and pyrrol has received important experimental demonstration from the researches of v. Baeyer, E. Fischer,* and Ciamician,† but up to the present time no material evidence has been accumulated to show that a similar relation exists between carbazol and pyrrol. The formation of carbazol from thio-diphenylamine‡ by the action of copper furnishes some proof in support of the formula given above; but as this is the only reaction clearly tending to show that carbazol is a di-ortho derivative of diphenyl, and, therefore, that it contains the pyrrol ring, further evidence in the same direction appears desirable.

In making the experiments which led up to the facts here recorded, I hoped to find points of resemblance between carbazol and pyrrol for which the >NH group alone, independent of the pyrrol ring, would not account, and thus to confirm indirectly the above formula of carbazol.

Runge, the discoverer of pyrrol, observed that its vapor in contact with pine moistened with hydrochloric acid,

* *Ber. d. chem. Ges.*, **19**, 2,988.

† *Ibid.*, **19**, 3,028.

‡ *Ibid.*, **20**, 232.

colored the wood intensely red. Von Baeyer subsequently described this reaction as being very characteristic of indol. It is interesting, therefore, to find that carbazol reacts similarly, though not so readily. In order to observe the reaction, soak the wood—an ordinary match-stem answers admirably—for a second or two in a hot alcoholic or acetic-acid solution of carbazol, and then thrust it into the neck of a bottle containing concentrated hydrochloric acid, so as thoroughly to expose it to the action of the gas without bringing it in contact with the acid solution. The red color soon develops, and slowly increases in intensity. The shade is precisely similar to that produced by pyrrol.

Since carbazol may be regarded as a derivative of indol in which the two carbon atoms of the indol ring are connected with the group C_4H_4'', this observation appears directly to contradict one of the deductions made by Emil Fischer* in the course of his study of indol derivatives. "The fir-wood reaction," he says, "no longer occurs when both the carbon atoms of the indol ring are connected with alkyls."

It seemed necessary, therefore, to confirm my results by substituting synthetical carbazol for that extracted from coal tar, with which I first obtained the reaction. In spite of careful purification, it is conceivable that the coal-tar carbazol might still retain traces of foreign substances capable of imparting to it the power of coloring the wood.

Through the kindness of Dr. A. Goske in forwarding to me a sample of carbazol recently obtained by him† by the action of copper on thio-diphenylamine, I have been able to confirm the results of previous experiments in a satisfactory manner.

It seems possible therefore that the di-alkyl derivatives of indol which do not, according to Emil Fischer, give the fir-wood reaction when the test is made in the usual way, may do so if the conditions of the experiment are somewhat varied.

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* *Ber. d. chem. Ges.*, **19**, 1,570.

† *Ibid.*, **20**, 232.

CARBAZOL AND ISATIN.

The behavior of thiophene (and furfuran) in forming coloring matters with isatin and ortho-diketones apparently similar to those of pyrrol, makes it probable that in such reactions the >NH group of pyrrol takes no part. Consequently, in the case of carbazol, as all the hydrogen atoms of the pyrrol ring, excepting that of the imide group, are already substituted, it is not to be expected that any similar coloring matters can be formed. For this reason I was surprised to find that the behavior of carbazol and isatin in the presence of sulphuric acid is such as to strongly suggest the indophenine reaction.

On adding concentrated sulphuric acid to carbazol and isatin, an intense blue color is developed as the substances dissolve. The reaction is extremely characteristic and can be used as a delicate test for the recognition of carbazol. The blue color of the solution does not appear to be affected by slightly warming, and even after standing some hours its intensity had not materially diminished or its color otherwise changed. Water precipitates an indigo-blue substance which very rapidly becomes lighter in color. In order to avoid this change, attempts were made to extract the blue coloring matter from the acid solution without the addition of water, by agitation with various solvents. These experiments proved unsuccessful, and the further study of the compound was abandoned.

Although the above is very like the indophenine reaction and its apparently analogous reaction in the case of pyrrol, I am inclined to believe, for considerations already mentioned, that the similarity is apparent only and not real. Diphenylamine gives no reaction with isatin under the same circumstances.

Since diphenylene-oxide and diphenylene-sulphide are probably related to furfuran and thiophene, respectively, in the same way as carbazol is to pyrrol, it seemed of importance to ascertain whether these substances also behaved similarly with isatin. I was unable to obtain any reaction with diphenylene-oxide, and consequently it is probable that diphenylene-sulphide also will be found indifferent.

CARBAZOL AND QUINONE.

The compounds produced from pyrrol and benzoquinone have no corresponding members in the thiophene series, and would appear to be directly or indirectly dependent upon the >NH group for their existence; it therefore seemed possible that carbazol and benzoquinone might react with the formation of similar compounds.

If a small quantity of sulphuric acid, diluted with one or two volumes of acetic acid, is added drop by drop to an acetic-acid solution of carbazol and benzoquinone, an intense carmine red solution is produced, which passes into a reddish-violet as the quantity of sulphuric acid is increased. Water precipitates from this solution a substance of the same color, which dissolves very readily in ether, chloroform and alcohol.

On the addition of crystals of quinone to carbazol dissolved in concentrated sulphuric acid, an intense green color is imparted to the solution. Hence, according to the strength of the acid used, a reddish-violet or a green solution is obtained.

Similarly Victor Meyer and O. Stadler* haves hown that benzoquinone reacts with pyrrol in two distinct ways. If aqueous solutions of the two are mixed, a violet coloring matter is produced, whereas in the presence of dilute sulphuric acid a green precipitate is formed. For purposes of comparison I repeated V. Meyer and Stadler's experiments. The violet coloring matter obtained dissolved in ether to a solution very similar in shade to that of the ethereal solution of the coloring matter from carbazol.

Before concluding that the formation of these compounds is in any way connected with the existence of the pyrrol ring, it seemed necessary to study the action of diphenylamine under similar circumstances. Sulphuric acid added to diphenylamine and quinone dissolved in acetic acid immediately colors the solution blue; on adding water, a violet substance is precipitated.

These reactions recall the coloring matters obtained by

* *Ber. d. chem. Ges.*, **17**, 1,035.

P. Greiff* by heating chloranil or quinone with methyldiphenylamine and other amines with or without the addition of zinc chloride. The similarity existing between the method of formation and the shade of Greiff's coloring matters and the violet compounds obtained as above described from pyrrol, carbazol and diphenylamine, renders it extremely probable that in both cases the coloring matters are perfectly analogous, and that their formation in the case of pyrrol and carbazol depends upon the amine character of these substances, and not upon the presence of the pyrrol ring. This view, which could not, unfortunately, be substantiated by analysis, owing to the great instability of the pyrrol compound, receives support from the fact already alluded to that thiophene gives no coloring matters with benzoquinone.

With reference to the green solution formed on adding quinone to carbazol dissolved in sulphuric acid, it seems probable that in this case quinone plays the part of an oxidizing agent only, for the same green-colored solution is produced, as is well known, by the addition of oxidizing agents generally under similar circumstances. It occurred to me, therefore, as not unlikely that quinone acts merely as an oxidizing agent also, when in contact with pyrrol in acid solution, especially as V. Meyer and Stadler extracted hydroquinone in considerable quantities from the mother-liquor after the green compound had been filtered off. Confirmation of this view was obtained by reference to Anderson's† description of the properties of pyrrol. He states that ferric chloride causes a dilute hydrochloric-acid solution of pyrrol to turn first *green* and then black. He adds that platinic chloride and potassic bichromate produce a black precipitate with the same solution.

A few experiments soon proved that not only ferric chloride, but potassic chromate or bichromate, platinic chloride, potassic ferricyanide, and even potassic nitrite under certain circumstances, all give, when added in small quantity

* *Ber. de chem. Ges.*, **12**, 1,610.

† *Ann. Chem.* (Liebig), **105**, 354.

to a dilute sulphuric-acid solution of pyrrol, a green substance which passes more or less rapidly, according to the oxidizing agent used and the acidity and degrees of concentration of the solutions employed, into the black compound observed by Anderson. With tolerably concentrated solutions of the oxidizing agents, the transition is so rapid that the green color can be scarcely observed, even when the sharpest lookout for it is maintained throughout the experiment.

With a dilute solution of potassic chromate, the formation of the green substance may be readily seen, and the reaction compared with that of quinone. As it is not easy, however, to obtain the reaction at its best without a number of trials, I prefer to give the exact strength of the solutions which I found to give good results. Eight drops of pyrrol are dissolved in 10 cc. of water to which eight drops of sulphuric acid have been added. When this is mixed with an 0·1 per cent. solution of potassic chromate in equal volumes, the green color is almost immediately developed, and rapidly increases in intensity until the solution becomes perfectly opaque. At this stage three or four volumes of water are added. The diluted solution is green in color, and slowly deposits a dark green or black precipitate.

A very dilute aqueous solution of quinone behaves almost precisely similarly with the above solution of pyrrol, but the precipitate formed is at first much greener than when potassic chromate is the oxidizing agent used. It gradually darkens, however, and after some hours becomes almost black. If the green precipitate from quinone is washed with an 0·05 per cent. solution of potassic chromate, it is very rapidly blackened.

From these experiments it would appear extremely probable, therefore, that quinone does not condense with pyrrol in acid solution, but merely acts like other oxidizing agents.

The formation of green substances like the above is not confined to the action of oxidizing agents on carbazol and pyrrol. It has long been known that nitrous acid and other oxidizing agents added in small quantity to diphenylamine

dissolved in sulphuric acid, produce an intense blue solution from which water precipitates a green compound; this, like the corresponding compounds from carbazol and pyrrol, is insoluble in ether.

PYRROL AND PICRIC ACID.

The behavior of indol and carbazol in combining with picric acid suggested the idea that probably pyrrol would form a similar compound. On adding picric acid to an excess of pyrrol, a red color is at once developed; on warming, the picric acid is dissolved, and the solution, when cold, deposits beautiful red needles. Similarly, if picric acid and an excess of pyrrol are dissolved in alcohol, long red needles, half or three-quarters of an inch in length, can be readily obtained as the solution is allowed to evaporate. The compound is very unstable, and commences to decompose in the air as soon as the crystals are dry. Its fusing point is about 71°. Since the basic properties of pyrrol are very weak, and no well-defined salts have been obtained with acids generally, the above described compound must be considered as analogous to the picric acid compounds of the hydrocarbons. The relation of pyrrol to benzol, so often dwelt upon by Victor Meyer, is thus once again emphasized. Phenyl-pyrrol also forms an unstable compound with picric acid. The compounds of pyrrol and its derivatives with picric acid will be further studied, and an attempt will be made to analyze them.

[COMMUNICATION.]

FOR SEALING OF VOLATILE LIQUIDS IN GLASS TUBES.

GENTLEMEN: The following communication on "The Sealing of Volatile Liquids in Glass Tubes," may be found of general interest. In order that glass tubes containing very volatile liquids may be properly sealed, the temperature of the tubes and their contents must be so lowered that the vapor tension of the liquid is not greater than the

atmospheric pressure. This is accomplished by immersing the tube in a cooling mixture to within a short distance of the point at which it is to be sealed. A tube containing liquid sulphur dioxide may thus be sealed while it is surrounded by a mixture of ice and salt.

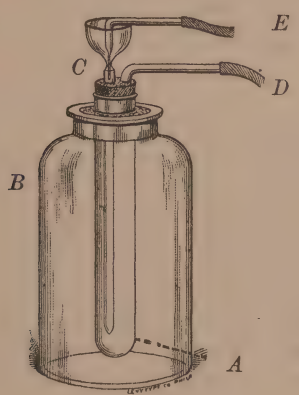
When the required temperature is below that of the ordinary freezing mixtures, advantage must be taken of the evaporation of liquid carbon dioxide or nitrous oxide at low pressures, and by care in manipulation it is then not difficult to seal tubes that are nearly filled with such volatile liquids as the two just named.

The tubes intended to contain such specimens, and which may be used to illustrate the phenomena of the critical condition and the precipitation of saturated vapors, must be made ready for sealing several days before they are to be filled, and carefully annealed in order that the glass may be prepared for the considerable pressure which it must sustain. Ordinary stout tubing with walls about two millimetres thick, and of five to seven millimetres internal diameter, may be employed. The piece selected is prepared by contracting the diameter to about two millimetres near one end, closing this end and blowing it into a funnel a little larger than necessary to hold all the liquid required to fill the tube. The other end of the tube is then sealed at the desired distance from the contraction—twenty centimetres is a convenient length. When the tubes have recovered from the effects of the heating, or immediately after they have been annealed in an oven, they are ready for filling and sealing.

The apparatus required for cooling the tubes during the operation is easily constructed, as shown in the accompanying diagram. A stout test tube, *A*, about twenty-five millimetres diameter, and of such length as is required by the tube to be sealed, passes through a flat cork in the mouth of a strong bottle, *B*, containing some pumice stone moistened with sulphuric acid. This test tube is half or two-thirds filled with liquid nitrogen monoxide or carbon dioxide, and about one-fourth as much ether is cautiously added. To the test tube is adapted a rubber stopper carrying the

tube *C* to be filled, the contraction at which it is to be sealed being about one centimetre above the level of the stopper, and a bent tube, *D*, the external end of which is connected with an aspirator.

The almost capillary extremity of a bent tube, *E*, is then passed through the contraction below the funnel, and through this the air is rapidly sucked from the tube as the liquid nitrogen monoxide is poured into the funnel. There must be sufficient space between the capillary tube and the walls of the contraction to allow the free descent of the liquid. When a sufficient quantity of liquid has been introduced, it is necessary to wait until the gauge of the aspirator



shows a constant pressure; the tube is then cut off at the contraction and sealed by directing on it the flame of a movable blast lamp. The tube *D* is then disconnected with the aspirator, and the sealed tube with the rubber stopper is carefully removed and placed vertically where its possible explosion on warming will do no harm. Pieces of bamboo cane, so cut that the joints form the bottom, make convenient receptacles for the tubes while they take the temperature of the room.

After the tubes have assumed the ordinary temperature, they should be gradually warmed to the highest degree to which they will probably be exposed, in order that there may be no risk in handling them.

If a mixture of nitrous oxide and ether be used for cooling, there should be no flame in the neighborhood of the recipient while it is open.

If the specimen be intended to illustrate the critical phenomena, the tube should be at least three-fourths filled with liquid before sealing. If it be designated to show the formation of a cloud and the precipitation of liquid drops, it should not be more than one-third filled.

I am indebted to Mr. Thos. R. Harrison for valuable assistance in preparing several tubes of nitrogen monoxide in the manner described.

Very truly,

Wm. H. Greene.

Central High School,
Philadelphia, December 1, 1888.

ABSTRACTS.

Reduction Products of Hæmatoxylin (J. Hegler. *Moniteur Scientifique* from *Jour. of Soc. of Dyers and Colorists*, **4**, 129).—Many attempts have been made to reduce hæmatoxylin, without satisfactory results.

Fr. Reim found that this coloring matter was not affected by sodium amalgam or zinc and sulphuric acid. On heating it with zinc powder, he obtained a crystallizable body, suspended in an oily liquid, but in too small a quantity to analyze it. Heavy gases were evolved at the same time, arising from the decomposition products, which could not be condensed.

E. Erdmann and G. Schultz have obtained, by heating hæmatoxylin in closed tubes with hydriodic acid, a mixture of hydrocarbons, which are partly volatile in steam and partly soluble in benzene.

C. Dralle, in confirmation of Fr. Reim's results, has detected the presence of carbonic acid and resorcin in the products of distillation.

The author's attempt to reduce hæmatoxylin with zinc powder also gave too small amounts of product to analyze.

The author tried the acetyl derivative obtained by the action of acetyl chloride. One part of the acetyl derivative of hæmatoxylin was gradually heated with thirty to forty parts of zinc powder in a slender tube under the air pump. The distillation product obtained in this manner consisted of resorcin in aqueous solution and a yellow oil, with a characteristic smell.

The author tried to separate the different products by fractional distillation.

The body, which passes over above 300° C., is solid, yellow, soluble in alcohol, ether, glacial acetic acid and benzene.

From these solutions it crystallizes in small yellow needles, grouped in stars, which fuse at 80°. This body forms a compound with picric acid which decomposes at 105°.

Three analyses gave the following results :

	Found.			*Calculated for.*		
	I.	II.	III.	$C_{15}H_{16}$	$C_{15}H_{14}$	$C_{15}H_{18}$
C.	90·82	90·58	90·71	91·82	92·78	91·42
H.	7·99	7·74	7·88	8·17	7·21	8·57

Owing to the small amount of substance obtained, it was not possible to have the hydrocarbon free from a small amount of a substance containing oxygen.

The vapor density determined by V. Meyer's method in sulphur vapor, together with the analysis, indicate the body to be a hydrocarbon $C_{15}H_{16}$, which is probably a homologue of diphenyl.

Vapor density—

Found.	*Calculated for.*		
	$C_{15}H_{16}$	$C_{15}H_{14}$	$C_{16}H_{18}$
6·88 and 6·72	6·79	6·72	7·27

The fraction between 200° and 300° passes over mostly at 250°–260°. It is a yellowish oil, with a strong smell, which turns brown in the desiccator over sulphuric acid. It is insoluble in alkalies, which is contrary to the character of a phenol.

On analysis it gave the numbers—

I.	II.
C = 88·24	87·93
H = 8·04	8·20

Its vapor density in sulphur was 5·59.

The portion passing over between 100° and 200° is a volatile liquid, with a penetrating odor, and is insoluble in alkalies. Unfortunately the author had too little substance to determine its vapor density.

On analysis the results indicated that it had the formula $C_{10}H_{14}O$.

	Found.		*Calculated for.*
	I.	II.	$C_{10}H_{14}O$
C.	80·79	79·79	80·00
H.	8·94	8·92	9·33

H. T.

On the Detection and Estimation of Magenta in Orchil and Cudbear. By Christopher Rawson (*Journal of Soc. of Dyers and Colorists*, **4**, 68).—The author has found such difficulties in the use of previously-published processes, that he suggests the following based upon the complete precipitation of the coloring matter of orchil or cudbear in an aqueous and alcoholic solution by acetate of lead, followed by an excess of ammonia. Magenta base under the same conditions remains in solution. From one to two grains of cudbear (or an equivalent amount of orchil liquor) are boiled with 50 cc. of alcohol, and afterwards diluted with 100 cc. of water; 15 to 20 cc. of a strong solution of basic acetate of lead (sp. gr. 1·25) are then added, followed after stirring by a similar quantity of strong ammonia. The mixture is filtered, and if the amount of magenta present is to be *estimated*, the precipitate is washed with a solution containing one part of ammonia,

five parts of alcohol and ten parts of water; otherwise the washing may be neglected. With pure cudbear, the filtrate is quite colorless; if magenta be present, it is either colorless or pink, according to the amount of ammonia present in the solution. The liquid is then acidulated with acetic acid, when the presence or absence of magenta is at once made apparent; in the case of pure cudbear or orchil, the solution remains colorless; whereas, if a salt of rosaniline be present, the well-known color of magenta is immediately developed. By means of this method one part of magenta in 100,000 of cudbear can be detected with certainty.

For determining the *amount* of magenta present the author suggests a calorimetric method, in which the filtrate or an aliquot portion of it is compared with a standard solution of magenta.

The method is also applicable to the detection of methyl violet and safranine. The base of the latter is much more soluble in ammonia than those of methyl violet and magenta.

The three coloring matters are distinguished from one another on the addition of acetic acid to the ammoniacal filtrate, the solution becomes of a bluish violet tint, if methyl violet be present. Under the same conditions, solutions of safranine and magenta are pink or bluish red. Strong ammonia decolorizes methyl violet and magenta, whereas it produces little or no effect upon a solution of safranine. Strong hydrochloric acid added to a solution of safranine, changes the color to a blue; solutions of magenta and methyl violet become, with the same reagent, of a pale yellow color.

The azo or oxy-azo dyes, as rocellin, orchil red, etc., when present in cudbear, may usually be detected by sprinkling a little of the sample on the surface of concentrated sulphuric acid, with the formation of a characteristic colored streak, which may be either green, blue or violet. To detect other adulterations, or in cases of doubt, one should resort to dye tests. H. T.

On the Preparation of Anhydrous Magnesium Chloride. Walther Hempel (*Berl. Ber.*, **21**, 897).—Anhydrous magnesium chloride is ordinarily made by the addition of ammonium chloride to the solution of the salt and the decomposition of the ammonio-magnesium chloride so formed by heating to about 460°. The author has found that the solution of magnesium chloride may be evaporated without decomposition and formation of basic salt, provided the operation be performed in an atmosphere of hydrochloric acid. The addition of ammonium chloride is unnecessary, and there is a great economy of heat. W. H. G.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, January 15, 1889.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, January 15, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Dr. L. B. Hall, Dr. H. W. Jayne, Dr. S. C. Hooker, Dr. Wm. C. Day, Dr. Wm. H. Wahl, Dr. S. P. Sadtler, Prof. Henry Trimble, Dr. H. F. Keller, Messrs. T. C. Palmer, W. L. Rowland, A. T. Eastwick, J. M. Newbold, Prof. R. L. Chase, Dr. Wm. H. Greene, Dr. D. K. Tuttle, and three visitors.

Mr. Pemberton, on taking the Chair, proposed a vote of thanks to the retiring officers for their efficient services.

The Committee on By-Laws reported progress.

The following gentlemen were elected members of the Section: Mr. F. C. Lewin, 1011 Spruce Street, Philadelphia; Mr. C. V. Petraeus, 231 South Front Street, Philadelphia; Mr. R. E. Fisher, 2239 St. Albans Place, Philadelphia; Dr. Wm. H. Greene, 204 North Thirty-sixth Street, Philadelphia; Dr. Geo. A. Koenig, University of Pennsylvania, Philadelphia; Mr. M. Carey Lea, 530 Walnut Street, Philadelphia; Prof. Henry Morton, Stevens Institute, Hoboken, N. J.

The following gentlemen were nominated for membership in the Section: Dr. T. R. Wolf, Newark, Del.; Mr. C. J. Semper, 505 South Forty-first Street, Philadelphia; Mr. S. Lloyd Wiegand, 146 South Sixth Street, Philadelphia; Prof. Edgar F. Smith, Ph.D., University of Pennsylvania; Mr. Marshall R. Pugh, University of Pennsylvania.

Dr. Wahl announced that papers read before the Section could be published in the JOURNAL OF THE FRANKLIN INSTITUTE, simultaneously with other journals, and that such articles would be continuously paged so as to form an independent work, which would be bound and issued as such by the Section.

The matter of obtaining a suitable desk for the benefit of the Secretary of the Section was referred to the conservator with power to act.

Notice was given by the President proposing an amendment to the By-Laws, making the annual dues $2 per year instead of $1 as heretofore.

The President appointed Drs. Greene, Hooker and Hall members of a Committee on Abstracts, the duty of the committee to consist in selecting from the various chemical journals articles to be abstracted, and in assigning such articles to the various members of a volunteer committee, by whom they are to be abstracted for the JOURNAL OF THE INSTITUTE.

Dr. Wahl announced the purchase of a complete set of the *Jahresbericht* for the Library of the INSTITUTE.

Dr. Hooker showed several specimens of the pyrrol, indol and carbazol groups, and spoke briefly on the relations of these compounds to each other. The "fir-wood" reaction was strikingly shown with pyrrol, phenyl-pyrrol and carbazol, and the best way of making it explained. Dr. Hooker called attention to the fact that pine was slowly colored bright green by concentrated hydrochloric acid. This he believed had not been previously observed. A pine splinter, moistened with an alcoholic solution of furfural, was also shown to turn intensely green when exposed to the action of hydrochloric acid gas, but this could be readily distinguished from the action of hydrochloric acid alone.

Adjourned.

WM. C. DAY, *Secretary.*

[*Erratum.*—In list of nominations for membership in December Proceedings, for Henry C., *read*, M. Carey Lea.]

REPORT OF THE CHEMICAL SECTION, FRANKLIN INSTITUTE, 1888.

MR. JOSEPH M. WILSON, PRESIDENT FRANKLIN INSTITUTE:

SIR:—I have the honor to submit the following report of the proceedings of the Chemical Section for the year 1888:

The work of the Section was carried on with the aid of the following

OFFICERS:

President—Mr. J. H. Eastwick.
Vice-Presidents—Prof. S. P. Sadtler, Mr. H. Pemberton, Jr.
Secretary—T. C. Palmer.
Treasurer—Mr. Chas. Bullock.
Conservator—Dr. Wm. H. Wahl.

Stated meetings were held on the second or third Tuesdays of February, May, June, September, October, November and December, and special meetings were held on April 24th and June 4th, making in all nine meetings during the year.

There has been a growing interest in the affairs of the Section on the part of members, and at the present time the indications of future development and increasing usefulness and importance are very marked.

The net increase of membership during the twelve months is nine, making a total of sixty-four members.

Several matters of importance have claimed the attention of the Section during the past year. Three subjects were submitted by the Committee on Science and the Arts, and reported upon by committees of the Section, to wit:

The reopened question of the Hyatt Pure Water Company's filtering apparatus, referred back on account of a protest against the award of the Scott Legacy Medal and Premium thereto; the Sodium Process of Mr. Hamilton Y. Castner, the Hydrogen Process for Preserving Iron and Steel.

These reports were forwarded to the Committee on Science and the Arts, and are now filed among their papers.

The further proceedings of the Section are given in abstract in the following record:

An arrangement has been made, whereby the proceedings of the Section shall be published in full, in successive numbers of the JOURNAL OF THE FRANKLIN INSTITUTE, and the minutes of the December meeting, together with several papers, have already appeared in the previous impression.

ABSTRACT OF PROCEEDINGS, 1888.

Stated Meeting, February 14th.—Dr. E. H. Keiser gave an account of his work on the estimation of the atomic weight of oxygen. The method followed was the burning of hydrogen occluded by palladium, and weighing of resulting water. Results showed $O < 15.96$. Adjourned.

Special Meeting, April 24th.—The Treasurer's report for 1887 was read. Bills were ordered to be paid. Resignations of Dr. J. B. Lober and Mr. Bruno Terne were accepted. Nominations of four gentlemen to membership were made. The deferred election of officers took place. The President announced the following committees: (1) *On the Castner Sodium Process*, Dr. E. H. Keiser, Messrs. Weikel and Palmer. (2) *On the Hydrogen Process for Preserving Iron and Steel*, Dr. Wm. C. Day, Messrs. Matos and Chase. Amendments to By-laws were announced. Dr. E. H. Keiser spoke further of his work on the atomic weight of oxygen. Further results had shown the probable correctness of the usually accepted number, 15.96. Adjourned.

Stated Meeting, May 15th.—The resignation as member of the Section of Mr. L. W. Moody was accepted. The committees appointed at last meeting reported progress, and were continued. Mr. Victor de Balas, Dr. D. K. Tuttle, Dr. Samuel C. Hooker, and Mr. Geo. C. Webster were elected to membership. The protest of Prof. A. R. Leeds against the report of a committee of this Section, on the Hyatt Pure Water System, together with said report and correspondence concerning the subject, was read, and, on motion, the matter was made a special order for an appointed meeting of the Section. Adjourned.

Special Meeting, June 4th.—The protest of Prof. A. R. Leeds against the favorable report of the Committee on the Hyatt Pure Water System, was read; also, the report in question, and various letters and documents bearing on the matter. After a very full discussion, it was

Resolved, That the Secretary be instructed to inform the Committee on

Science and the Arts, that the Chemical Section, acting as Committee of the Whole, has carefully considered the protest of Prof. A. R. Leeds against the award of the Scott Legacy Premium and Medal to the Hyatt Pure Water Company, and does not deem the evidence submitted of sufficient importance to warrant it in recommending a re-opening of the question.

Dr. E. H. Keiser read the report of the Committee on the Castner Sodium Process. The report concludes with the following: "It appears, from all the evidence submitted to us, that, through the efforts of Mr. Castner, an advance step has been taken in the manufacture of sodium, which cannot help having a beneficial effect on industry." The report was adopted. Dr. Wm. C. Day read the report of the Committee on the Hydrogen Process for Preserving Iron and Steel. This report contained a description of the process, but stated that the committee had been unable to obtain any evidence of its successful working. Accepted. Adjourned.

Stated Meeting, June 19th.—Bills for printing were ordered to be paid. Dr. H. W. Jayne read a paper on "Coal Tar Products." The paper was illustrated by numerous specimens and drawings. The lecturer spoke particularly of the present state of manufacture and various uses of naphthalin, giving many facts and circumstances of great interest. On motion of Prof. N. W. Thomas, a vote of thanks was tendered Dr. Jayne for his unusually interesting paper. Adjourned.

Stated Meeting, September 18th.—Routine business and general discussion. Adjourned.

Stated Meeting, October 16th.—Dr. Samuel C. Hooker read a paper on "Estimation of Nitrates in Natural Waters, and Some New Reactions of Carbazol." A general discussion of the paper followed. Adjourned.

Stated Meeting, November 20th.—Two gentlemen were nominated for membership in the Section. Treasurer was authorized to receive subscriptions to JOURNALS for the year 1889. Nominations of officers for the year 1889 were made. Mr. H. Pemberton, Jr., spoke of a constant error found by him in a line of burettes made by Greiner, of New York, due to the graduation having been made with the aid of mercury, the meniscus of which is different from that of water. Dr. Jayne described the extensive color works at Basle, and laboratories connected with them; spoke also of the vast extent of the color market in China and Japan, due to the practice of household dyeing. The commercial peculiarities of the color trade of Europe were also described. Miscellaneous discussion. Adjourned.

Stated Meeting, December 18th.—Two gentlemen were elected members of the Section, and seven nominated. The following were elected officers for 1889:

President—Mr. H. Pemberton, Jr., 1947 Locust Street, Philadelphia.

Vice-Presidents—{ Dr. S. C. Hooker, Franklin Sugar Refinery, Phila.
Mr. T. C. Palmer, 22 North Front Street, Philadelphia.

Secretary—Dr. Wm. C. Day, Swarthmore College, Delaware County, Pa.

Treasurer—Dr. H. W. Jayne, Bermuda Street, Frankford, Philadelphia.

Conservator—Dr. Wm. H. Wahl, FRANKLIN INSTITUTE, Philadelphia.

Mr. Pemberton presented a communication from Dr. Wahl, concerning the publishing of papers of the Section. Committee to confer with Dr. Wahl, Mr. Pemberton, Jr., Dr. S. C. Hooker. Committee to revise By-laws and membership list: Mr. T. C. Palmer Dr. H. W. Jayne, Prof. R. L. Chase. Mr. Lüthy exhibited and remarked on the mineral eudialyte. Prof. Chase and Dr. Jayne discussed the film of the Welsbach gas burner. Dr. Hooker showed samples of so-called electrically refined sugar. Mr. Luthy agreed with him in his estimate of the alleged electric process. Mr. Macfarlane exhibited a souvenir of the twenty-fifth anniversary of the color works of Meister, Lucius & Bruening. Dr. Hooker showed a sample of saccharin and described the most reliable test for it. Discussion of the wholesomeness of saccharin, by Dr. Hooker, Dr. Jayne, Dr. Hall. Adjourned.

Respectfully, T. C. PALMER, *Secretary.*

ON THE ASH OF TILLANDSIA USNEOIDES.

BY T. C. PALMER.

[*To be read before the Chemical Section*, FRANKLIN INSTITUTE, *February 19, 1889.*]

At the suggestion of Prof. H. Trimble, I have made an analysis of the ash of Florida long moss, with results that are perhaps worthy of publication.

About the year 1835, Avequin of New Orleans, published* an analysis of this ash, in the following terms:

1,000 grammes of moss gave 32·35 grammes ash.

[Ash = 3·235 per cent.]

Composed of—

	Grammes.
Salts of potash (phosphate, sulphate, carbonate, chloride),	11·47
Lime, partly as carbonate,	5·96
Phosphates of lime and magnesia,	9·26
Silica containing a little iron and manganese,	5·66
	32·35

This seemed to be the only analysis hitherto made of the ash, and it is very incomplete.

The results obtained by me are given as the average of two concurring analyses, and are as follows:

* *Journal de Pharm. et Chimie*, iii, **35**, 95.

Total ash, 2·95 per cent., the dried plant.

PERCENTAGE COMPOSITION.	*Per Cent.*
SiO_2,	10·3000
Fe_2O_3,	2·100
Al_2O_3,	2·600
MnO,	1·672
CaO,	12·700
MgO,	11·351
K_2O,	13·759
Na_2O,	14·856
SO_3,	7·419
Cl,	6·947
CO_2,	12·900
P_2O_5,	3·034
Total,	99·638

It is rather difficult to compare these two analyses, on account of the difference in the way they are recorded; but in the two cases where I have tried grouping some of the constituents in the manner of Avequin, the agreement is close enough to show that in all probability, nearly identical results have been reached in the two cases. So far as it goes, this is proof of the *à priori* idea that the ash of this plant is practically, and within certain limits, uniform, regardless of where it grows. Avequin gathered his sample near New Orleans; that selected for the above analyses came from Florida.

It is my desire to point out that here we have an anomaly of a certain sort. *Tillandsia* is a typical epiphyte, and according to definition should select its mineral matter, as well as its organic matter, entirely from the air. Its roots are not supposed to give it any nourishment, being merely anchors or grippers.

But unless the floating dust of the forests where this plant grows is more plentiful and more complicated in composition than we have any reason to think it, what we know of the circumstances of *Tillandsia's* growth points, in the light of these analyses, to an absorption from the trees on which it grows, of the mineral constituents at least. The presence of manganese oxide to the extent of 1·672 per

cent. of the total ash, is especially significant, for manganese has come to be looked on as a very common constituent of vegetable growths in general.* Thus it is found in notable quantities in wheat, edible roots, such as potatoes, in peas and beans, in tobacco, tea, coffee, fruits, etc., and not accidentally, but uniformly. But especially in point is the fact that manganese is very plentiful in the barks of various species of trees. Thus, two samples of the bark of *Quercus tinctoria* gave each a total ash of about three per cent. and of this, in each case, about 1·5 per cent. was manganese oxide. An extract of hemlock bark (*Abies Canadensis*) gave a total ash of 2·5 per cent., of which manganese oxide constituted 5·128 per cent. An extract of quercitron bark gave an ash of 4·98 per cent., of which 3·740 per cent. was manganese oxide. These few examples might be continued indefinitely, but they will suffice to show the abundance of manganese in barks; and, further, its presence in the extracts of the barks shows it to be in a soluble form in the barks. The other constituents are such as one finds in the bark of trees; and no single one of them is entirely anomalous in a plant. So that it would appear that *Tillandsia* does probably get its mineral food like other plants, from the earth and not from the air.

The crucial test, however, remains to be made, and I shall proceed to make it. That will consist in the analysis of some *Tillandsia* that has been grown on a support incapable of affording any mineral matter already in solution, such as a glass rod. Such an analysis will be the subject of another paper.

ABSTRACTS.

On the Behavior of the Hydrates and the Carbonates of Barium and of the Alkali Metals at High Temperatures.—By Prof. W. Dittmar (*Jour. Soc. Chem. Ind.*, **7**, 730). A description of the carbonates and hydrates of the above bases when highly heated in an atmosphere of hydrogen, of nitrogen, and of carbon dioxide. *Carbonate of lithia*, heated partly by Bunsen burner, partly by gas blow-pipe, for thirty-seven hours, in atmosphere of *hydrogen*, gave a residue analyzing $Li_2O = 99·57$ per cent., and $CO_2 = 0·6$ per cent., showing practically a complete decom-

* Maumene. *Bull. Soc. Chim. de Paris*, **42**, 305.

position, into oxide, due principally to the action of the hydrogen, but partly to mere dissociation, as the following experiment shows: Li_2CO_3 heated in an atmosphere of *nitrogen* to highest temperature for one hour, gave residue containing 7·77 per cent. Li_2O. Heated in same manner for ten hours, residue contained 30·37 per cent. Li_2O. Even in an atmosphere of carbon dioxide, the Li_2CO_3 was slightly decomposed, showing traces of Li_2O; and this, too, at a temperature barely sufficient to keep the substance in a state of fusion. An interesting result, however, was obtained by heating Li_2CO_3 in CO_2 to a red heat, *under a pressure* varying from one slightly above the normal to a full extra atmosphere (in boat in a porcelain tube). The mean of several closely agreeing experiments gave a residue containing *more* CO_2 than required, if we accept Stas' atomic weight of 7·02; the atomic weight, in fact, so deduced, being 6·909. The Li_2CO_3 used was carefully purified, but the presence of any possible impurities would have had no bearing on the argument, as the effect of such would have been to make less CO_2 present; not more.

Lithium hydrate, crystallized ($LiHO + H_2O$), lost in dry hydrogen all crystal water at 100°; the LiHO remaining undecomposed up to 320°. Heated to redness in H for four hours completely reduced to Li_2O. Crystallized *barium hydrate*, heated in hydrogen to red heat, gave in four hours pure BaO.

Barium carbonate, heated in *hydrogen* two hours by Bunsen burner, then five hours by gas blow-pipe, gave residue containing only 0·1 per cent. CO_2.

2·2168 grammes of the same, strongly heated in muffle in atmosphere of *nitrogen* for one hour, lost only 1·9 m'grs., showing great differences in the behavior in hydrogen and in nitrogen.

Sodium carbonate, heated in hydrogen, loses CO_2, leaving mixture of hydrate and carbonate, the amount of hydrate formed in four hours, by blow-pipe, varying from 11·9 to 20 per cent. Heated two hours in nitrogen residue, contained of sodium monoxide 1·759 per cent., showing slow dissociation at a red heat.

Potassium carbonate gave similar results, but with formation of smaller quantities of hydrate. The same may be said of *rubidium carbonate*. This latter salt was heated for two hours over gas blow-pipe; when the crucible was opened, it was found to be empty, showing the great volatility of Rb_2CO_3. A table of solubilities of lithium hydrate is given; also, a description of modification of Liebig's bulbs, by which loss by splashing is prevented, in passage of a quick stream of CO_2. P.

A NEW PROCESS FOR OBTAINING AMMONIUM CHLORIDE FROM THE NITROGEN OF COAL, COKE, CINDERS AND ORGANIC MATTER GENERALLY. —By Andrew French. (*Jour. Soc. Chem. Ind.*, **7**, 735.) A paper well worthy of attention. A large pile of furnace cinders, containing half-burned coal, and which had been drenched with salt water, caught fire. A stream of waste water from a fume condenser saturated with sulphurous acid was run upon it, and, in a few weeks, the fire extinguished. The interesting result of this was the formation of a large quantity of chloride of ammonium.

"It is no exaggeration to say that the surface of the heap was for the greater part covered with white, sparkling sal ammoniac, as if with snow, and, at one time, a ton at least of that salt might have been collected. In some places there were large cakes of it from an inch to an inch and a-half thick."

On digging into the heap after the fire was extinguished, an abundance of sodium sulphate was found, but scarcely any sodium chloride.

Following the advice of Prof. Dittmar, the author, tried the following experiments:

A sample of similar ashes, drenched with salt water, was burned in a Cornish assay furnace with a supply of steam, SO_2, and a limited amount of air; resulting in the profuse production of NH_4Cl. No NH_4Cl was formed if either the salt, SO_2, or steam was omitted.

Again, the nitrogenous substance was mixed with salt and iron pyrites, and made into a little brick with clay (free from N). This was then heated in a porcelain tube, and steam and air together passed through it. The following are some of the results obtained:

	Pounds NH_4Cl Per Ton.
Black's Slamanan coal,	129·6
Clyde Company's Ell coal,	101·2
Clyde Company's Jewel coal,	138·8
Coal *cinders* (coke),	96·8

Experiments on the large scale were then tried with the spent shale from a mineral oil works, in a small kiln, also with coal in the furnaces of steam boilers, using from five hundredweights to five tons of coal in the various tests, and in all cases a large yield in sal ammoniac was obtained. The author quotes several authorities, showing that the production of ammonium chloride in burning coal mines had been observed more than half a century ago. It was in 1884 that he made the observations above described, but it does not appear from this paper, that any systematic application on an industrial scale has since been made. P.

Double Bromide of Copper and Ammonia in Photography. L. L. de Koninck (*Zeitsch. f. angewandte Chemie*, **88**, 507).—Bromide of copper is sometimes applied for correcting over-exposed plates. It is, however, not easily prepared, and the commercial salt is often insoluble and has not the desired effect. The author, therefore, recommends in its stead the double salt of cupric bromide and ammonium bromide, which is easily obtained in the following manner:

A weighed quantity of copper fragments are introduced into a glass-stoppered bottle and covered with about twice their weight of water. Bromine is then added by degrees under frequent shaking, until all copper is dissolved as well as any white cuprous bromide which first forms, and bromine is present in small excess.

Occasional cooling is advisable in order to prevent loss of bromine. The dark red solution is transferred to a porcelain dish and heated until the small excess of bromine is evaporated. To the remaining solution of cupric bro-

mide a corresponding quantity of ammonium bromide is now added in the relation of 2 mol. NH_4Br to mol. Cu, *i. e.*, 195·5 AmBr for 63·3 Cu or 309 for 100. After filtration the solution is evaporated to crystallize. The crystals are emerald green and well formed. The concentrated solution of this salt is wine red, the dilute like that of most copper salts, faint bluish green. A solution of 1 : 1,000 of this double salt acts with great energy upon photographic silver pictures, an over-exposed picture disappearing within a few moments. O. L.

Filtration and Purification of Colloid Precipitates by Diffusion. E. Bauer (*Chemiker-Zeitung*, *1888*, *789*) recommends for this purpose a funnel, the lower part of which has been cut off, so that the apex of the paper filter reaches down into a body of water (or other solvent) contained in a beaker. By repeated changing the water and covering the precipitate the latter is finally completely washed. O. L.

A New Alkali Process.—By W. W. Staveley (*Jour. Soc. Chem., Ind.*, **7**, 807). During the last half century many attempts have been made to decompose sulphate of sodium by means of slaked lime. Even in very dilute solutions and under a high pressure, however, only a small proportion of the sodium sulphate can be so decomposed; the reason being the comparatively great solubility of sulphate of lime, in connection with the sparing solubility of calcium hydrate. The author finds, however, that by the addition of *cresol* (C_7H_8O; one of the phenols existing in oils from coal) about ninety-five per cent. of the sodium sulphate is decomposed. Any of the phenoloids may be used, those distilling between 190° and 250° C., however, being most suitable. As a practical illustration of the process, eleven hundredweights of quick-lime are slaked and sufficient water added to make a volume of, say, 400 gallons. When cold, about 430 gallons of distilled phenoloids are added, and the mixture gradually run into, say, 900 gallons of a solution of ninety-five per cent. sodium sulphate, containing about twenty-nine and three-fourths hundredweights of the latter. The mixed solutions are now agitated for several hours, at a temperature of 30° to 40° C. About ninety-five per cent. of the Na_2SO_4 has now been decomposed, with the formation of thirty-two and one-half hundredweights of $CaSO_4$, $2H_2O$. The latter is allowed to settle and the solution of sodium phenolates run off, the calcium sulphate being washed on a filter. The sodium phenolate solution is now treated with carbon dioxide (from furnace fires or from lime-kiln); the phenoloids thereupon are liberated and separate as an oily fluid, floating on the surface of the sodium carbonate solution. They can now be used over again for decomposing a new lot of Na_2SO_4, as before. The Na_2CO_3 solution still contains about one per cent. of its bulk of phenoloids, and, to prevent their being carried off with the steam on evaporation, a little caustic soda is added. The Na_2CO_3 is then, after evaporation, separated as "fished salts," in the usual way, the phenoloids remaining in the red liquor (or rather in what would correspond to the red liquor, as in this case, there are no sulphides present), and are, of course, united with the main quantity

separated previously. The fished salts are calcined as usual and sold as soda ash.

By this process phenoloids are lost, (1) by mechanical adherence to the "fished salts," and (2) by retention in the calcium sulphate precipitate; the latter loss being the more important. The total loss amounts to about twenty gallons of phenoloids per ton of Na_2CO_3 produced. By using oils containing phenoloids, instead of the distilled article, the cost of the phenoloids proper would be about five pence per gallon. The net result of all of which being that about $2 worth of phenoloids must be added afresh for each ton of soda ash made. There appears to be no difficulty in obtaining an abundant supply of the oils at the above figure.

The process is, of course, as applicable to potassium salts as to sodium, and the sulphites may be used, when possible, instead of the sulphates.

The whole idea has been developed so far only on a small scale, but the above paper, in which it is described (of eight pages length), excited much interest. The application of organic compounds to the soda industry is a new departure. P.

On the Molecular Weight of Aluminium Compounds.—Roux and Louise (*Bul Soc. Chim.*, **50,** 497), have determined the vapor densities of aluminium methyl and aluminium ethyl by Victor Meyer's method in an atmosphere of nitrogen. Within 40° of the boiling points of the substances, the densities correspond exactly with the formula Al^2X^6; they then gradually diminish, and the decrease is due to decomposition of the vapors. The fact of decomposition was shown by passing the vapor of aluminium ethyl through a glass tube heated to 380°, the walls of the tube then becoming lined with a deposit of aluminium. By the method of Raoult, ethylene bromide being employed as a solvent, the molecular weights found for the ethyl, propyl and isoamyl compounds of aluminium, correspond with the molecular formula Al^2X^6. W. H. G.

On the Preparation of Concentrated Formic Acid.—M. Maquenne (*Bul. Soc. Chim.*, **50,** 662) recommends that dilute formic acid (45–50 per cent.) be concentrated by distillation with an equal weight of concentrated sulphuric acid under reduced pressure. The acid so obtained is about eighty-five per cent. pure; loss three per cent. A second distillation of this product, with half its weight of sulphuric acid, gives an acid of ninety-eight per cent., the loss being six per cent. The temperature must not be raised above 75°, and the quantity of sulphuric acid employed must be less than that which, with the water of the formic acid, would yield the crystallizable hydrate, $H^2SO^4 + H^2O$. The formic acid retained by the sulphuric, and which constitutes the loss, may be recovered by diluting with water and redistilling. W. H. G.

On the Rapid Analysis of Water for Industrial Uses, with a View to its Chemical Purification.—Leo Vignon (*Bul. Soc. Chim.*, **50,** 598) determines the uncombined carbonic acid by a standard solution of calcium hydroxide, so finding the amount of lime necessary to saturate the

free acid. The quantity of sodium carbonate required to throw down as carbonates the soluble salts of calcium and magnesium is then estimated by the aid of a standard sodium carbonate solution. In each case phenol-phthalein is employed as an indicator. W. H. G.

On the Detection of Salicylic Acid in Beer.—H. Elion (*Recueil de Travaux Chimiques*, **7**, 211) recommends that the beer be shaken with two or three times its volume of ether; after separation of the latter liquid it is agitated with a small quantity of slightly alkaline water. If salicylic acid be present in quantities of five to ten grammes per hectolitre, and the operation be performed on 100 cc. of beer, the reaction of salicylic acid with ferric chloride is sufficiently marked in the aqueous liquid after acidifying with hydrochloric acid. If much smaller proportions of the acid be present, the acidified aqueous liquid should be shaken out with ether, and the test made on the dry residue after evaporating the ether. The author also describes a satisfactory method for the estimation of salicylic acid. W. H. G.

Potassium Metabisulphite.—J. M. Eder (Phot. Corresp., **25**, 416 from *Journ. Soc. Chem. Ind.*). Potassium metabisulphite (K_2SO_3, SO_2) is used in place of sodium-hydrogen-sulphite to preserve pyrogallol solutions. It is prepared by saturating a solution of potassium carbonate with sulphurous anhydride and adding alcohol. The salt separates as a white crystalline powder and is washed with alcohol.

Citric Acid in Cow's Milk.—F. Soxhlet (*Bied. Centr.*, **17**, 787–788). G. T. Haekel has confirmed the existence of citric acid, as calcic citrate, in normal milk. The examination of many samples shows the presence of about 0·1 per cent. citric acid. A good cow yields daily, therefore, as much citric acid as is contained in two or three lemons. S. C. H.

Report on the Chemical Constitution of Natural Gas.—F. C. Phillips. (From the *Official Report of the Geological Survey of Pennsylvania*). A number of samples of gas taken from various borings in the oil region consisted essentially of hydrocarbons of the paraffin series, with about nine to fifteen per cent. nitrogen.

Carbon dioxide was present in all the samples in small quantities (fractions of one per cent.), and ammonia, oxygen, sulphuretted hydrogen and hydrogen were found in traces in some instances.

Of the hydrocarbons, methane predominates; numbers of unsaturated series are entirely absent.

One hundred cubic feet of the gas was found to have a heating effect, varying with the different samples, equivalent to from seven to nearly nine pounds of pure charcoal. S. C. H.

The Absorption of Gases by Petroleum.—S. Gniewosz and A. Walfisez. *Zeitsch. f. Phys. Chem.*, **1**, 70. (From the *Journ. Soc. Chem. Ind.*) The coëfficient for the absorption of oxygen and many other gases by

petroleum is much higher than that for water. The authors consider it, therefore, illusory to try to protect liquids from oxidation by covering them with a layer of petroleum.

Constituents of Sugar Cane.—Winter. (*Zeitsch. f. Zuckerind*, 1888, 780. The author states that levulose is not present in normal ripe sugar cane, and that the leaves, while containing cane sugar and glucose, are also free from levulose. Hence, he concludes that the assumption that cane sugar is formed by the condensation of levulose with glucose is no longer tenable. Other constituents of the cane were also examined. S. C. H.

The Plastering of Wine in France.—Report of the United States Commercial Agent, at Limoges. *Board of Trade Journal*, 1888, 439. The addition of sulphate of lime to wine is known as "plastering." It is said that by this means the fermentation is increased, rendered more rapid and complete, and that the wine, while improved in color, has its keeping properties enhanced. Acid sulphate of potash is thus virtually substituted for the bitartrate of potash. Free sulphuric acid is formed in wines which have been plastered. The Academy of Medicine, at Paris, is now discussing whether the practice is desirable, and what effects the changes induced by the sulphate of lime on the mineral constituents of wine are likely to have upon the health of the consumer. S. C. H.

On the Occurrence of Boric Acid in Wine.—Georg Baumert, *Berichte*, **21**, 3,290. The author confirms the observations of Ripper & Soltsien with regard to the occurrence of boric acid in the leaves and wood of the vine; and like these chemists insists that boric acid must in future be regarded as one of the normal constituents of the ash of wine. A large number of wines from San Francisco, Spain, France and Germany were examined. S. C. H.

On Pyrodine. a New Antipyretic.—J. Dreschfeld. *Medical Chron.*, **9**, 89–99. From the *Journ. of Soc. Chem. Ind.* The active ingredient of pyrodine is acetyl-phenyl-hydrazine C_6H_5,N_2H_3,C_2H_3O. It is a white almost tasteless, crystalline substance, possessing more powerful antipyretic properties than either antipyrine, antifebrine or phenacetine. Dose, two to four grains for children; eight to twelve for adults. It should not, as a rule, be given oftener than once in eighteen to twenty-four hours, on account of its toxic properties, but as the temperature is kept low for a longer period than by the use of other substances this is very rarely necessary. S. C. H.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, February 19, 1889.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, February 19, 1889.

Dr. SAMUEL C. HOOKER, Vice-President, in the Chair.

Members present: Dr. L. B. Hall, Dr. H. W. Jayne, Dr. Wm. H. Wahl, Dr. E. H. Keiser, Dr. H. F. Keller, Prof. Henry Trimble, Prof. E. F. Smith, Messrs. W. L. Rowland, F. C. Lewin, A. T. Eastwick, Marshall R. Pugh, T. C. Palmer, Dr. W. C. Day, and a number of visitors.

An abstract of a letter from Prof. Ira Remsen, editor of *The American Chemical Journal*, was read. The letter requested first publication of papers read before the Section.

The Committee on By-Laws, Mr. T. C. Palmer, Chairman, submitted a report, which was read and approved. Accompanying the report was a copy of the revised By-Laws, which was read; a few changes were made and, in order to give time for the full consideration of the By-Laws, they were laid over until the next meeting for final action, the Secretary being instructed to have them printed and to send a copy to each member of the Section.

A report from the Treasurer was read and, in connection therewith, it was recommended that certain delinquent members should be notified that unless arrears be made good their names would be dropped from the list of members; it was also recommended that such notification should be given in all similar cases occurring in future.

The following gentlemen were elected members of the Section: Dr. T. R. Wolf, Newark, Del.; Mr. C. J. Semper, 505 South Forty-first Street, Philadelphia; Mr. S. Lloyd Wiegand, 146 South Sixth Street, Philadelphia; Prof. Edgar F. Smith, Ph.D., University of Pennsylvania; Mr. Marshall R. Pugh, University of Pennsylvania.

Mr. F. Lynwood Garrison was nominated for membership in the Section.

The motion that the annual dues be increased from one dollar to two dollars, the initiation fee remaining one dollar, as heretofore, was carried.

The resignation of Mr. Robert Frazer was accepted.

Mr. T. C. Palmer's paper, "On the Ash of *Tillandsia Usneoides*," a copy

of which was already in the hands of all the members, was read by title. The author requested that those who might be able to contribute information or give reference to papers on this subject would kindly do so, as he is still occupied with the investigation of the way in which this plant obtains its mineral nourishment.

Dr. H. F. Keller then read a paper "On Diacetyl and Some of its Derivatives;" which has been referred for publication.

Diacetyl was first produced by heating ketipic acid, which splits up into carbon dioxide and a yellow volatile liquid which proved to be diacetyl. The facts upon which the structure of this substance is based were considered, as well as the methods of preparation, composition and properties of a number of its derivatives.

Dr. Hooker showed a specimen of benzil, the compound in the aromatic series which corresponds to diacetyl.

Dr. Wahl gave a brief account of some interesting experiments, upon which he is now engaged, in connection with the electrolysis of hydrochloric acid. In electro-plating with platinum and iridium, a number of difficulties present themselves; the solution of metal constantly varies in strength, owing to the fact that the metal is dissolved only in insignificant quantity at the anode, so that the metallic strength of the plating solution is constantly being weakened, requiring frequent additions to be made to the bath. Another difficulty is that the deposit is spongy, black and non-adherent in character, rather than reguline and bright. The first difficulty has been overcome by Dr. Wahl, and he is now working with special reference to the second, with encouraging prospects. Dr. Wahl expects to bring before the Section, in the near future, a paper which will consider in detail his experiments and their results. Professor Smith described a method of determining platinum electrolytically by depositing the platinum from the compound, K_2PtCl_6, on a platinum dish (previously plated with copper), by means of a low current applied for five or six hours; the presence of sulphuric acid is advisable. No platinum could be detected in the liquid after the action. Dr. Wahl then exhibited some specimens of his platinum and iridium plating, which were inspected with much interest by the members.

The Secretary exhibited a specimen of highly bituminous coal from a new source in Alaska.

Adjourned.

WM. C. DAY, *Secretary.*

ABSTRACTS.

CAYOTA, A NEW TANNIN. M. Villou (*L'Ind. Text.* and *Textile Colorist*, **11** 8).—This reddish-brown bark comes from the southern part of Mexico, where it is used for tanning thick sole-leather, to which it is said to impart "strong consistency and great solidity." It is easily powdered, has a resinous odor, and according to Mr. Ebertz, of Berlin, contains twenty-two to thirty per cent. of tannin. The pure tannin, separated by the author, consists of yellow scales, which dissolve in fifteen parts of their weight of cold water, and

in all other solvents for tannin. It colors the salts of iron a fine black, whose intensity is variable according to whether the decoction or extract of the bark is obtained in the cold, or by boiling under pressure or in the presence of oxydizing agents. Its molecular weight is equal to that of the tannin from oak bark. The bark or extract is said to be superior to Quebracho on account of the absence of resin, and to give to silk the suppleness of sumac.

H. T.

On the Detection of Caustic Alkali in the Presence of Alkaline Carbonates. L. Dobbin (*Jour. Soc. Chem. Ind.*, December 31, 1888, pp. 829–830).—This method depends on the coloration of dilute solutions of potassium iodide in mercuric chloride, to which ammonium chloride has been added. This reagent gives no coloration or precipitate with sodium or potassium carbonate, but forms a delicate test for caustic alkali, a yellow coloration being produced as soon as a sufficient quantity has been added to change the whole of the ammonium chloride present into potassium salt and free ammonia. By using a reagent containing a very small proportion of ammonium chloride the test is extremely delicate. The quantity of caustic alkali is estimated by color comparison.

M. R. P.

On Some Abnormal Samples of Butter. A. H. Allen (*Analyst*, January, 1889).—Professor Stein, official analyst to the Danish government, having been led to doubt how far the limits generally adopted by public analysts in the examination of butter were to be relied on, an investigation was ordered by the Royal Agricultural Society, and the author invited to take a part in it. Average butter fat takes by the Reichert-Wollery process 29·2 cc. $\frac{n}{10}$ alkali, whereas butter from one of the farms inspected, which had been so closely watched as to render adulteration impossible, took but 24·7 cc., and that from another but 22·3 cc. $\frac{n}{10}$ alkali. Although these butters are exceptional, yet they were produced from the milk of a large number of cows, so it cannot be said that such butter may not be met in practice. Nilson, of Stockholm, found the volatile acids to vary materially with the time since calving. The author also discusses the detection of vegetable oils. In conclusion he recommends that a committee of the Society of Public Analysts receive and tabulate results of analysis, and devise, if possible, some method of examining butter less dependent on the natural variations in its composition, than the methods at present in use.

M. R. P.

Artificial Coffee. A. Stutzer (*Zeitschr. für Angewandte Chemie*, 1888, p. 699).—The author calls attention to the manufacture of artificial coffee and of machines for that purpose as carried on by certain firms in Cologne. The following analytical results of the artificial product were obtained by O. Reitmair:

	Per Cent.
Moisture,	8·30
Extract soluble in hot water,	34·34
Insoluble organic constituents,	56·26
Inorganic material,	1·10

A microscopic investigation showed that the bulk of the artificial coffee

consists of burnt flour or meal. According to Reitmair, the artificial beans (which are well formed) may be distinguished from the genuine by the fact that the former immediately sink when immersed in ether, while the genuine, on account of the fat contents, float, in great part, on the surface. Furthermore, genuine coffee beans are much more rapidly decolorized by the action of hot, strong oxidizing agents (such as aqua regia or $HCl + KClO_3$) than the artificial. In detecting adulteration of coffee by the artificial article both of these methods of testing should be carried out as preliminary measures. W. C. D.

SALICYLIC ACID FOR PRESERVING EGGS. Lambert (*Arch. de Pharmacie*, 1888, 440).—A solution of salicylic acid is not to be recommended for keeping eggs in preference to lime-water. The acid diffuses through the shell and may be readily detected on the white of the egg. S. C. H.

A GERMAN patent (D. R. P. 45,857) has been granted to A. Doutrelpont, for a process of preparing a new explosive, "Petragit," from molasses. It is an oily nitro-product, and is said to have three times the power of nitro-glycerine. S. C. H.

THE ANALYTICAL EXAMINATION OF WATER FOR TECHNICAL PURPOSES. Alfred H. Allen (*Journ. Soc. Chem. Ind.*, **7**, 795).—The results given by the soap test when water contains considerable quantities of magnesium compounds in addition to lime salts are very misleading. A water, containing both lime and magnesia, does not destroy so much soap as the same amounts of lime and magnesia would do separately. The author speaks strongly against further employment of the soap test, unless some means can be found of counteracting the disturbing action caused by magnesium salts. It seems probable that calcium carbonate sometimes exists in a soluble colloid form, which is changed on boiling to the insoluble modification. The author is still investigating the subject. S. C. H.

TRICHLORACETIC ACID is said to be the best and quickest escharotic yet known for warts, corns and bunions (*Merck's Bull.*, 1, **5**, 1888). S. C. H.

HYDROXYCYANIDE OF MERCURY is likely to take the place of corrosive sublimate. It does not attack the metal of surgical instruments, and in some cases shows six times the bactericidal power of corrosive sublimate (*Merck's Bull.*, 1, **5**, 1888). S. C. H.

ON TWO NEW CHLORIDES OF INDIUM, AND ON THE VAPOR DENSITY OF THE CHLORIDES OF INDIUM, GALLIUM, IRON AND CHROMIUM. L. F. Nilson and Otto Petterson (*Ann. Chim. Phys.*, **6**, xv, 545).—The only chloride of indium heretofore known is obtained by heating the metal in an excess of chlorine. According to C. and V. Meyer's determinations of its vapor density, it has the formula $InCl_3$. The experiments of the authors confirm this. By heating indium in a current of dry hydrochloric acid gas a chloride, $InCl_2$, is formed, which, though very stable at high temperatures and when kept dry, is imme-

diately decomposed by water, thus, $3InCl_2 = 2\,InCl_3 + In$. The dichloride, when heated with an excess of In, forms a monochloride InCl, a red substance resembling hematite. This, like $InCl_2$ is decomposed by water, $3InCl = InCl_3 + In_2$. The correctness of the formulæ of both the new chlorides is amply established by their vapor densities. Experiments were also made to ascertain the true formulæ of the chlorides of gallium and chromium, which lead to the acceptance of $GaCl_2$, $GaCl_3$, $CrCl_2$, $CrCl_3$. The so-called sesquichlorides of gallium and chromium must, therefore, in future be expressed by the simpler formulæ, $GaCl_3$, $CrCl_3$. The formula of ferrous chloride, $FeCl_2$, was confirmed.

S. C. H.

Researches on Cobalt and Nickel. Gerhard Krüss and F. W. Schmidt (*Ber.*, **22**, 11).—The authors were engaged in re-determining the atomic weights of nickel and cobalt, by Winkler's method. A weighed quantity of the metal was immersed in a solution of chloride of gold, and the amount of the gold thus expelled determined. In spite of many experiments the results obtained did not agree with the values, as determined by Zimmermann or Winkler, and it was found on closer examination that the precipitated gold contained a small quantity of cobalt (or nickel). In order that this might be removed the precipitate was dissolved in aqua regia, and after the excess of acid had been expelled, the gold was re-precipitated by sulphurous acid. The difference in weight of the gold before and after purification was deducted from the weight of the cobalt (nickel or) taken. Even with this precaution the results obtained were not constant.

On washing gold which had been first precipitated by cobalt, and subsequently by sulphurous acid, it was observed that the last washings were somewhat green. This portion of the filtrate was evaporated to dryness; the residue, after ignition, dissolved on heating in concentrated hydrochloric acid, giving rise to a beautiful green solution, which became almost colorless on cooling. With nickel, the same was observed. The reaction, clearly, was not that of any known substance, and, as in both cases, the amount obtained was extremely small, experiments were started in the hope of extracting larger quantities. This has been successfully accomplished by the authors in several ways.

(1) By repeatedly treating precipitated sulphide of nickel with ammonic sulphide, the nickel was gradually dissolved and the ultimately insoluble residue was found to contain considerable quantities of the desired body.

(2) By crystallizing solutions containing corrosive sublimate and chloride of nickel (or cobalt), the double chlorides separate and the new substance could be obtained from the mother liquor.

(3) By treating the oxides of cobalt and nickel with fused alkalies, the oxide of the new body alone dissolves. In this way about two per cent. of the pure oxide may be obtained from oxide of nickel.

The new oxide gives the following reactions: Ammonic sulphide causes a black precipitate from neutral solutions; ammonia, a white, voluminous precipitate insoluble in excess. The chloride is white when pure, but in contact

with strong hydrochloric acid is greenish. The chloride, but not the oxide, is reduced to a black metal at a red heat.

The following, having reference to the above, is an extract from a letter written by Dr. Krüss, and published in the *Chemical News* of January 25th:

"I have in fact succeeded in splitting up nickel and cobalt each into two parts, and both these metals have one component in common. In concert with my colleague I sent a brief notice on this subject to the *Berichte*, which will appear in Berlin on Monday next (the above is abstracted from the paper here referred to). The matter communicated in this short memoir has been intentionally kept very scanty, and I gave as little room as possible to speculation for fear of being led to assertions which I might, perhaps, soon have to withdraw. Meantime, I have fully confirmed our first observations, and we have now about ten different methods by which we can resolve these bodies, hitherto regarded as elementary, each into two parts. We shall soon give a full report on our results, but in the meantime I may inform you, as a curious fact, that we have succeeded in obtaining *green* so-called nickel salts from *red* cobalt salts and the *colorless* salts of the substance which accompanies both metals, and farther, in transforming some green nickel salts into red cobalt salts and other components. This may sound alchemical, but it cannot be denied. As for the spectra of the three components of cobalt and nickel, we have not yet, with the ordinary experimental arrangements, observed any characteristic lines. This is doubtless the reason why hitherto no spectral lines have been found common to pure cobalt and nickel."

S. C. H.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, March 19, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, March 19, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Dr. L. B. Hall, Dr. H. W. Jayne, Dr. E. H. Keiser, Dr. H. F. Keller, Dr. Wm. H. Wahl, Prof. R. L. Chase, Prof. E. F. Smith, Dr. S. C. Hooker, Messrs. Reuben Haines, T. C. Palmer, W. H. Bower, Thos. N. Newbold, C. J. Semper, Jacob Lichenheim, W. L. Rowland, F. Lynwood Garrison, W. W. McFarlan, Dr. W. C. Day, and three visitors.

The revised By-Laws, which had been laid over at the last meeting, were adopted without alteration.

The Treasurer reported that, in accordance with a recommendation made at the previous meeting, he had notified certain delinquent members of their arrears; as a result arrears were made good in one case, while in four others they were not; the Section voted that the names of the four delinquent members be dropped from the list.

Mr. F. Lynwood Garrison was elected a member of the Section.

In accordance with the new By-Laws, Section VII, the President appointed Messrs. W. W. McFarlan, W. H. Bower and the Secretary members of the committee to transact the financial business of the Section.

Upon nomination, in accordance with the revised By-Laws, Section II, the following gentlemen were elected members of the "Committee on Admissions": Dr. L. B. Hall, Dr. E. F. Smith, Dr. H. F. Keller, Dr. Wm. H. Wahl, Dr. S. C. Hooker, Mr. W. L. Rowland and Mr. C. J. Semper.

At the close of the meeting the Committee on Admissions notified the Secretary that Mr. Lee K. Frankel and Mr. A. W. Allen had been elected members of the Section.

Upon the motion of Dr. Jayne, it was voted that 250 extra copies of the revised By-Laws be printed for the future use of the Section.

Mr. T. C. Palmer then read his paper on "The Testing of Logwood Extracts."

Mr. Palmer remarked that he wished to call particular attention to the statement in his paper, that under the conditions of the test for strength of logwood extracts, with which the paper dealt, the compounds of tannin and copper oxide were nearly or quite colorless. This difference in behavior between tannin and hæmatine was the more remarkable, since in many other respects the latter acts precisely as a tannin. This is even true with respect to its action on hide powder. An attempt to estimate the tannin in a pure extract of logwood, by means of filtration through powdered hide, had resulted in an apparent showing of twenty per cent. of tannin, which loss was evidently due to an absorption of the hæmatine by the hide. In fact, the attraction of the hide for the coloring matter is quite as strong as it is for tannin. The speaker here showed a column of hide powder deeply colored by the passage through it of a very dilute clear solution of logwood.

Mr. Palmer also made some preliminary remarks on the faultiness of the tannin process of Hammer, as modified by Procter, giving data that show the amount of soluble matter in hide powder to depend very largely on the time the water is in contact with the hide, *i. e.*, in the rate of percolation. The hide powder, made by Schuchardt, gave to water an extract that left a residue on evaporation, ranging in amount, easily oxidizable, soluble in water, and with many of the reactions of the so-called coriin. The one fact above all that showed the faultiness of the process of Procter was that this residue, when redissolved in water, *was precipitated on addition of tannin solution.* Thus while the amount soluble in water could be only roughly estimated, the amount dissolved out by the tannin solution was simply unknowable, since at the top of the column, where the tannin is in abundance, there would be no dissolving out of the coriin, but as the liquor trickled down, losing tannin, it would dissolve more and more. The speaker stated that he expected shortly to bring before the Section his method of obviating this difficulty, retaining hide powder as the absorbent of tannin, but obtaining the tannin strength of the solution before and after filtration by an expedient that rendered evaporation of solutions or specific gravity determinations unnecessary.

Dr. S. C. Hooker's paper, "On a Rapid Colorimetric Method of Accurately Determining Nitrates in Potable Waters," was read by title.

Dr. E. H. Keiser read a paper "On the Redetermination of the Atomic Weight of Palladium." The following is an abstract of this paper, which was listened to with much interest, and was afterwards discussed by a number of the members present:

The atomic weight of palladium has not been determined very carefully. The only data for the calculation of this constant, at the present time, are two analyses of the double chloride of palladium and potassium, made by Berzelius in 1828. These two analyses do not agree very well. The first one gives 105·7, and the second one 106·2 for the atomic weight of palladium.

For the purpose of redetermining this atomic weight, metallic palladium in the form of foil was dissolved in aqua regia and the solution evaporated to dryness. The palladium chloride was then dissolved in dilute hydrochloric

acid and the solution was filtered. Ammonia was added to the filtrate until the precipitate, which at first formed, was redissolved. After filtering the solution again, to remove any traces of ferric hydroxide, the filtrate was saturated with hydrochloric acid gas. The palladium is thus precipitated as palladium-diammonium chloride, $Pd(NH_3Cl)_2$, a yellow crystalline compound which is insoluble in water and acids, but which is readily soluble in dilute ammonia.

The yellow precipitate was redissolved in dilute ammonia, and the solution was filtered. If any rhodium had been present in the original sample of metallic palladium, it would have been separated by this process, because the rhodium diammonium chloride is insoluble in dilute ammonia. The filtrate was thereupon treated with hydrochloric acid and the palladium diammonium chloride, thus precipitated, was thoroughly washed with distilled water, until all ammonium chloride was removed. The compound was carefully dried over sulphuric acid in a partial vacuum.

The compound was analyzed by weighing off portions in platinum boats and heating up in a current of pure hydrogen. At a low temperature the yellow compound absorbs hydrogen, metallic palladium and ammonium chloride being formed.

$$Pd(NH_3Cl)_2 + H_2 = Pd + 2\,NH_4Cl.$$

On raising the heat, the ammonium chloride is completely volatilized and spongy palladium remains behind. After the boat and its contents had cooled off somewhat, the hydrogen stream was replaced by one of dry air, and the boat was allowed to cool off completely in the air. By this means it was possible to avoid the retention of hydrogen by the palladium, and as the hydrogen stream was not displaced by air until the temperature of the palladium had fallen considerably below a low red heat, it was not possible that palladium oxide should have been formed.

Determination of Atomic Weight of Palladium.

I.—By ignition of $PdN_2H_6Cl_2$ in current of hydrogen.

Number.	Weight of Substance.	Weight of Palladium.	Atomic Weight.
1,	·83260	·41965	106·459
2,	1·72635	·86992	106·410
3,	1·40280	·70670	106·355
4,	1·57940	·79562	106·342
5,	1·89895	·95650	106·321
6,	1·48065	·74570	106·292
7,	1·56015	·78585	106·322
8,	1·82658	·92003	106·317
9,	2·40125	1·20970	106·355
10,	1·10400	·55629	106·400
11,	·93310	·47010	106·366
Total,	16·74583	8·43606	[106·3520]

Atomic weight = 106·35 H = 1· Maximum, = 106·459
N = 14·01 Minimum, = 106·292

Cl = 35·37 Difference, = ·167

Atomic weight = 106·62, when o = 16.

The foregoing table contains the results of all of the determinations that were made.

The investigation will be continued. It is intended to make a series of determinations by means of other palladium compounds.

Prof. E. F. Smith followed with two interesting papers, the first of which was entitled, "Oxidations by Means of the Electric Current," and the second, "On the Compound $C_{21}Cl_{26}$." Both papers were referred for publication in the JOURNAL OF THE INSTITUTE.

In connection with the use of the electric current in determining and separating metals, it occurred to the author that the oxidizing power of the current might be utilized to convert sulphur and other elements into higher oxides, thus securing them in forms susceptible of ready determination. Chalcopyrite was placed in a nickel crucible, containing fused potassium hydroxide. In connection with the positive pole of a battery, a heavy platinum wire from the negative pole was introduced just under the surface of the fused mass. The current was continued for ten minutes, when the contents of the crucible were dissolved out, filtered from insoluble oxides, acidified with hydrochloric acid and treated with barium chloride, when it was found that all the sulphur contained in the mineral was precipitated as barium sulphate. Comparative experiments, using the above method and also that of oxidizing with nitric acid, gave with the former method 32·35 per cent. sulphur in a specimen of chalcopyrite, and with the latter method 32·54 per cent. sulphur. The strength of the current used was one ampère.

Chromite treated in the same way as chalcopyrite yielded a little more than fifty-three per cent. Cr_2O_3 in a specimen which an older method of determination had shown to contain fifty-four per cent. Cr_2O_3.

Further experiments in this line are in progress.

The second paper, by Dr. Smith and Dr. H. F. Keller, called attention to a remarkable compound of carbon and chlorine, first produced by Dr. Smith in 1876, by the exhaustive action of chlorine on toluene exposed to sunlight, first at the boiling point and then in the cold. Analysis showed 21·41 per cent. carbon and 78·6 per cent. chlorine. The substance was crystallized from chloroform, yielding crystals measuring one-half inch in length and one-fourth inch in breadth and apparently orthorhombic.

Crystals of this compound originally melting at 152 to 153° C. were preserved for twelve years, and at the end of that time no visible alteration had taken place, but on taking the melting point this was found to have changed to 101° C., at which it remained constant after recrystallization from pure chloroform. On heating a portion of the substance in a test tube hydrochloric acid was evolved; a combustion gave 22·8 per cent. carbon and 2·2 per cent hydrogen. Work is now going on to prepare the chloride again and to determine its vapor density as well as to study some of its derivatives. The authors wish to reserve this field of investigation for the present.

Dr. Jayne exhibited some specimens of commercial anthracenes. He stated that at present it is rarely made in the United States, as there was no market for any large quantity of the hard pitch which would be obtained in distilling tar for anthracene and as all produced would have to be sold

abroad, it was only made by a couple of firms, and then only when prices were high.

About twenty per cent. more of the tar was distilled off than when soft pitch was made, the distillate after cooling is filtered by means of a filter press. The resulting soft cake contains from ten to fifteen per cent. of anthracene, depending on the quality of the tar, the temperature of the oil and the pressure employed in filtering. This is then generally pressed in hydraulic presses, the percentage of anthracene then rising to about twenty-five to thirty per cent. This can be still further increased by treating with solvents, coal tar, naphtha, benzine, creosote oil, etc. The impurities partly dissolving and on re-pressing the residue an anthracene of about forty-five per cent. could be obtained. Recently it has been proposed to use as a solvent a mixture of solvent naphtha and the pyridine basis of coal tar; from such a solvent, it is said, anthracene of eighty per cent. can be obtained commercially. The process is said to be in operation in Germany in two factories.

The crude anthracene is not generally purified further by the tar distillers, but sold as such to the alizarine makers. The presence of any quantity of paraffines renders anthracene unsalable, as it interferes greatly with the subsequent treatments in the alizarine manufacture.

In England they are classed as A and B qualities.

A quality is an anthracene made from New Castle coal and is more valuable as it contains less paraffines.

B quality is made from Lancashire and Yorkshire coals, but it is customary to rate all anthracene not from New Castle coal as B quality, without further examination, for this reason American anthracene is considered of B quality.

It is sold at a certain price per unit or percentage of real anthracene it contains.

For instance, the present price in London is about thirty cents per unit per hundred-weight for A quality and twenty-six cents for B.

Therefore A anthracene of forty-five per cent. or units is worth 30×45 or $13.50 per hundred-weight and B quality $11.70.

The per cent. is generally determined by the amount of anthraquinone produced under certain conditions, the method being known as the "Hoechst" test. A weighed quantity dissolved in glacial acetic acid is oxidized by a solution of chromic acid in acetic acid. The resulting anthraquinone, after washing and drying, is dissolved in sulphuric acid of 1·88 on the water bath and, after complete solution, precipitated by water, and weighed, then burned and the resulting ash deducted.

Prof. R. L. Chase called attention to an article on the industrial use of oxygen in bleaching; he was requested to prepare an abstract of it for the JOURNAL.

Adjourned.

WM. C. DAY, *Secretary.*

On Diacetyl and Some of its Derivatives.*

By Harry F. Keller.

[*A paper read before the Chemical Section at the Stated Meeting, February 19, 1889.*]

With a view to a synthetic formation of citric acid, Fittig and Daimler† subjected ethyl oxalate to the action of ethyl monochloracetate and zinc. The reaction did not take place in the desired manner, but they found among the products the ether of a dibasic, diketonic acid, which they termed ketipic (diketoadipic) acid. From the reactions of this ether it appeared highly probable that the structure of the acid must be expressed by one of the two formulæ:

$$\begin{array}{ll} CO,CH_2COOH & CO,CH_2,COOH \\ CO,CH_2COOH & CH_2,CO,COOH \end{array}$$

It was observed that upon heating the acid was decomposed into carbonic dioxide and a yellow volatile liquid. At the suggestion of Professor Fittig I undertook the study of this reaction, in the hope of arriving at a definite conclusion in regard to the structure of ketipic acid. The former of the two formulæ given above proved to be correct: ketipic acid is readily split up into diacetyl and carbonic anhydride according to the equation:

$$\begin{array}{l} CO,CH_2,COOH \\ CO,CH_2,COOH \end{array} = \begin{array}{l} CO,CH_3 \\ CO,CH_3 \end{array} + 2CO_2$$

Diacetyl is the simplest orthodiketone of the fat series, a class of compounds for the production of which a great many fruitless attempts had been made. Since the discovery of its formation from ketipic acid, diacetyl has been obtained by two other reactions, viz: (1) By v. Pechmann‡ on treating isonitroso methylactone successively with acid

* From the *Inaugural Dissertation for the Degree of Doctor of Philosophy*, Strassburg, 1888.

† *Ber.*, **20**, 202.

‡ *Ber.*, **20**, 3,162.

sulphites of the alkalies and dilute sulphuric acid, and (2) by L. Wolff,* who found that it was formed by boiling β-dibrom-laevulinic acid with water.

The constitution of diacetyl is deduced from the following facts:

(1) Its empirical formulæ is $C_4H_6O_2$.

(2) It combines readily with two molecules of phenylhydrazine, of hydroxylamine and of hydrocyanic acid. It must, therefore, contain twice the carbonyl group.

(3) As the dicyanhydrin yields dimethyl racemic acid, the two carbonyl groups must be directly united.

Preparation.—In order to obtain a sufficient quantity of diacetyl for investigation, it was necessary to prepare large quantities of ketipic ether. In the beginning the method described by Daimler † was strictly adhered to, while later it was found more convenient to prepare it according to W. Wislicenus' ‡ reaction from ethyl acetate, ethyl oxalate and metallic sodium. The ether was converted into the free acid by treating it in the cold with hydrochloric acid, saturated at 0°; small quantities of it that had escaped saponification were removed by boiling the dry powdered product with chloroform, in which the acid is insoluble.

From this acid diacetyl can be obtained either by destructive distillation, or by boiling with dilute sulphuric acid.

In decomposing ketipic acid in the dry way, it was found necessary, for obtaining a satisfactory yield of the diketone, to distil *small* quantities, not exceeding five grammes at a time and to heat rapidly. The escaping vapors and gases were passed through a U-tube, provided below with a collecting bulb, and at the farther limb with an inverted condenser. The U-tube and bulb were placed in ice. The heating is continued until white fumes cease to come off. In the receiver there collects a liquid which consists of two layers; the upper one, which is of an oily appearance, is almost

* Private Communication.

† *Inaug. Diss.*, Strassburg, 1886.

‡ *Ber.*, **20**, 590.

pure diacetyl, and the lower one an aqueous solution of it. They were separated by means of a tap funnel, and sodium chloride added to the watery solution. Diacetyl and very little water passed over first on distillation. The oily layers were then united, dried with neutral chloride of calcium and fractioned. The by far greater portion distilled over between 85° to 89°, and but a small reddish-brown residue of empyreumatic odor remained in the bulb. The distillate showed a much lighter color than the original product; it was again treated with chloride of calcium, and then distilled over completely between 87°·5 and 88°.

The decomposition of ketipic acid is also readily effected by heating with dilute sulphuric acid (1:10). A violent evolution of carbonic anhydride is observed when the liquid is heated to near its boiling point, and great care must be exercised in regulating the temperature in order to avoid serious losses. The aqueous distillate is treated as described above.

The yield never exceeds fifty per cent. of the theory; it is about the same for both methods.

All attempts to obtain the monocarboxylic acid of diacetyl by splitting off only one molecule of carbonic acid were unsuccessful.

Diacetyl is a mobile liquid of an intensely yellow color and characteristic odor. It boils without decomposition between 87°·5 and 88°; the vapor is greenish yellow, resembling chlorine. Its specific gravity is 0·9734 at 22°. It is soluble in four parts of water at ordinary temperature and is miscible with alcohol and ether in all proportions.

I. 0·2563 grms. gave 0·5207 grms. CO_2 and 0·1632 grms. H_2O
II. 0·2150 " " 0·4390 " " " 0·1386 " "

	Calculated for $C_4H_6O_2$	*Found.* I.	II.
C	55·81	55·40	55·68
H	6·98	7·07	7·16

Diacetyl prepared by the reactions of v. Pechmann and of L. Wolff was found, on comparison, to be identical in every respect with that from ketipic acid.

Diacetyl shows all the reactions which are peculiar to the ketones.

It combines with the acid sulphites of the alkalies with the evolution of heat. The compound formed was not isolated, as it did not crystallize out of the solution upon standing.

When sulphurous anhydride is passed into an aqueous solution of diacetyl, its smell and color rapidly disappear; nothing can be extracted from the solution by shaking with ether. No sulphuric acid is produced by the reaction and on evaporating the liquid over sulphuric acid *in vacuo* diacetyl is regenerated. It is probable that a loose combination of the diketone with SO_2 exists, which breaks up as soon as the excess of the latter is removed.

Osazone of Diacetyl.—

$$\begin{array}{l} CH_3.C{=}N.NHC_6H_5 \\ \quad\quad | \\ CH_3.C{=}N.NHC_6H_5 \end{array}$$

On adding 2 mols. of phenylhydrazine to the ethereal solution of 1 mol. of diacetyl, the osazone separates out on standing in the form of beautiful yellowish needles. This compound is insoluble in most of the ordinary solvents, soluble with difficulty in $CHCl_3$, somewhat more readily in acetone, and in boiling benzol. It was obtained pure by recrystallization from the latter as a light yellowish powder, melting at 239°, with decomposition.

I. 0.3017 grms gave 0.8009 grms. CO and 0.1882 H_2O
II. 0.2213 " " 0.5870 " " " 0.1401 "
I. 0.2579 " " 46.5 cc. N at 17°.5 and 751 mm.
II. 0.2133 " " 39.2 cc. " 18° " 750 mm.

	Calculated for $C_{16}H_{18}N_2$	*Found.* I.	II.
C	72.18	72.38	72.32
H	6.76	6.93	7.03
N	21.06	21.02	21.38

Dioxim.—

$$\begin{array}{l} CH_3{-}C{=}N{-}OH \\ \quad\quad | \\ CH_3{-}C{=}N{-}OH \end{array}$$

This compound is formed by mixing aqueous solutions of diacetyl and of hydroxylamine hydrochloride, which has pre-

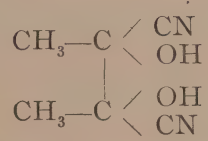
viously been neutralized with carbonate of sodium. It is precipitated white, in the form of microscopic needles. It is insoluble in water, readily soluble in alcohol and ether, and melts with partial sublimation at 234°·5. By boiling it with dilute sulphuric acid, diacetyl is again produced.

0·2380 grms. gave 0·3606 CO_2 and 0·1525 grms. H_2O
0·2278 " " 45·7 cc. N at 8° and 759 mm.

	Calculated for $C_4H_8N_2O$	*Found.*
C	41·38	41·32
H	6·90	7·11
N	24·14	24·48

A compound prepared by Schramm* in the laboratory of V. Meyer several years ago, was found to be identical with this dioxim, after a redetermination of the melting point.† It had not been analyzed.

Dicyanhydrin.—

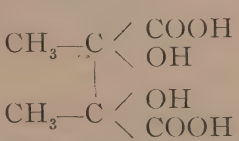


This is obtained by adding diacetyl to an excess of prussic acid in aqueous solution. The mixture is gently warmed for some time and then extracted with ether. On evaporation of the latter, the nitrile remains in the form of colorless needles or prisms, united to peculiar dendritic shapes. It is soluble in water, alcohol and ether, insoluble in all other solvents. It is very hygroscopic and decomposes when heated with water. It melts at about 110°.

0·3189 grms. dried in the desiccator gave 57·9 cc. N at 19° and 734 mm.

	Calculated for $C_6H_8N_2O_2$	*Found.*
N	20·00	20·58

Dimethylracemic Acid.—



* Schramm, *Ber.*, **16**, 179.

† Private communication of Professor Meyer to Professor Fittig.

Strecker* has observed that racemic acid is formed upon boiling glyoxal, prussic acid and dilute hydrochloric acid. It was, therefore, to be expected that diacetyl, under similar conditions, would give dimethylracemic acid.

An acid of the composition $C_6O_6H_{10}+H_2O$, and whose properties closely resemble those of racemic acid, was obtained by slightly modifying Strecker's method. It was prepared in the following manner: The finely powdered crystals of the hydrocyanide were placed in a small flask and covered with concentrated hydrochloric acid; it passed slowly into solution, but on standing, colorless crystals were observed to separate; they probably represent the acid amide. No attempt was made to determine their character, but the mixture was first heated and then the hydrochloric acid evaporated on the water bath; the residue was dissolved in water and the solution divided into two equal parts. Of these one was exactly neutralized with K_2CO_3, and boiled; the other portion was then added. Upon cooling, the acid potassium salt—which, like that of tartaric acid, is difficultly soluble—crystallized out. This was recrystallized, then converted into the neutral salt and the solution of this precipitated with acetate of lead. The lead salt was washed with water, dried, pulverized, and then suspended in water and decomposed with hydrogen sulphide. On evaporating the filtrate, the new acid crystallized out in large, shining prisms and plates. These have the habitus of crystals of racemic acid. They contain 1 mol. of H_2O, but do not effloresce in the air. The acid is readily soluble in water and in alcohol, insoluble in ether.

0·2494 grms. of air dry acid gave 0·0227 grms. loss and 0·3361 CO_2 and 0·1177 CO_2

	Required for $C_6H_{10}O_6$ H_2O	*Found.*
C	36·73	36·75
H	5·10	5·24
H_2O	9·18	9·10

The anhydrous acid melts at 180°; it is decomposed at this temperature. Heated on platinum foil, it is decom-

‡ *Zeitschrift f. Chem.*, 1868, 216.

posed and completely volatilized without leaving a trace of carbon.

Böttinger* has described, as dimethyltartaric acid, an acid which he obtained as a side product by the action of zinc upon an alcoholic solution of pyruvic acid. It showed no tendency to crystallize, undoubtedly because it was impure; its salts are certainly identical with some of those described below.

Potassium Salts.—The neutral salt is obtained from the acid one by exact neutralization with potassium carbonate. It is quite soluble in water, and crystallizes in needles.

The acid salt, $C_6H_9O_6K$, the preparation of which has been described above, is readily soluble in hot water, sparingly in the cold. It crystallizes in crusts or little plates. It contains no water of crystallization.

0·2526 grms. gave 0·1008 grms. K_2SO_4.

	Required for $C_6H_9O_6K$	*Found.*
K	18·05	17·92

Calcium Salts.—$C_6H_8O_6Ca + 1\frac{1}{2}$ HO.† Chloride of calcium throws down from solutions of the neutral salts of the alkalies a white crystalline precipitate, insoluble in water and acetic acid.

0·2653 grms. lost on heating to 215–220° 0·0282 grms. H_2O, and gave 0·1483 grms. $CaSO_4$.

	Calculated for $C_6H_8O_6Ca \cdot 1\frac{1}{2}H_2O$	*Found.*
H_2O	11·11	10·64
Ca	16·46	16·43

Barium Salt.—$C_6H_8O_6Ba + H_2O$. Although quite as insoluble as the calcium salt, this is not precipitated immediately by barium chloride or acetate, it separates out completely, after some time, in the form of small needles, which

Annalen*, **188, 315.

† Both the Ba and Ca salt were dried in the desiccator before they were analyzed; for this reason the Ba salt was found to contain less H_2O than Böttinger determined.

are generally grouped around a common centre. It contains 2 mols. of water, which are driven off at 160°.

0·2046 grms. gave 0·0211° loss and 0·1364 grams $BaSO_4$.

	Required for $C_6H_8O_6Ba + 2H_2O$	*Found.*
Ba	39·25	39·19
H_2O	10·32	10·31

The lead salt is precipitated in the form of a voluminous precipitate on adding lead acetate to the neutral potassium salt solution. It is likewise insoluble in water and in acetic acid. From acid solutions it is obtained in small needles.

In addition to the reactions described, the solution of potassium dimethylracemate gives the following: $ZnSO_4$ produces a white amorphous precipitate, insoluble in water and dilute acetic acid. $AgNO_3$ in concentrated solutions gives a white curdy precipitate. With ammoniacal silver solutions a metallic mirror is formed, especially on warming.

$HgCl_2$ throws down a white precipitate.

$CuSO_4$ is colored deep blue by the solution; the liquid remains clear on adding alkalies.

Ferric chloride produces a voluminous yellowish brown precipitate.

Halogen Derivatives of Diacetyl.—Bromine acts upon diacetyl but slowly in the cold; on warming two atoms of hydrogen are replaced. Dibromdiacetyl is best prepared by adding bromine dissolved in CS_2 or $CHCl_3$ to a similar solution of the diketone, until the red color no longer disappears on heating in the water bath. The solvent is then distilled off and the residue repeatedly crystallized from carbon disulphide and from petroleum ether. Thus obtained it forms yellow leaflets of a waxy lustre, melting at 117°. It is soluble in ether, carbon disulphide, chloroform and petroleum ether.

I. 0·2 grms. gave, after treating with Na amalgam, 0·3083 grms. AgBr.
II. 0·2 " " " boiling " Na_2CO_3 solution, 0·3079 grms. AgBr.

	Calculated for $C_2H_4Br_2O_2$	*Found.* I.	II.
Br	65·57	65·59	65·51

It is probable that the two atoms of bromine are attached to two *different* carbon atoms, as the action of Br

does not seem to proceed any further, even when a large excess is added.

Monochlordiacetyl.—By the action of chlorine upon diacetyl in the sunlight, a thick oily liquid, possessing the color of diacetyl and a pungent smell, was obtained, it did not crystallize at — 12°. Its boiling point is about 150°. Sodium carbonate solution decomposes it, especially on heating.

0·5656 grms. gave, after treating with Na_2CO_3, 0·6566 grms. AgCl.

	Required for $C_2H_3O_2Cl$	*Found.*
Cl	29·46	28·72

The further study of the halogen derivatives of diacetyl is being proceeded with.

Metallic Compounds.—When diacetyl is added to a solution of silver nitrate with *just* enough ammonia to hold the oxide of silver in solution, metallic silver is precipitated, sometimes as a mirror upon the glass; if on the other hand a large excess of ammonia be used, a voluminous white precipitate is formed, even in extremely dilute solutions of the diketone. A similar precipitate forms in ammoniacal solutions of cuprous chloride.

After drying them at 100°, these substances were analyzed with the following results:

Ag compound:

I. 0·234 grms. gave 0·2874 CO_2 and 0·892 H_2O and 0·1153 Ag.
II. 0·2368 " " 0·2898 CO_2 and 0·0923 H_2O
III. 0·294 " " 0·1442 Ag

	Required for $C_6H_9N_2Ag$	*Found.* *I.*	*II.*	*III.*
C	33·18	33·46	33·37	
H	4·14	4·23	4·33	
Ag	49·77	49·28		49·04

Copper compound:

I. 0·2123 grms. gave 0·3216 CO_2 and 0·1030 H_2O
II. 0·4335 " " 58·6 cc. N at 15·5° and 755 mm.
III. 0·2008 " " 0·091 CuO

	Required for $C_6H_9N_2Ag$	*Found.* *I.*	*II.*	*III.*
C	41·86	41·39		
H	5·23	5·35		
N	16·27		16·32	
Cu	36·62			36·14

These compounds are quite stable; at high temperatures they are decomposed with formation of acetamide.

They are evidently salts of the trimethyl glyoxaline, discovered by v. Pechmann.* This was proved also by preparing the hydrochloride of the base, by decomposing the salts with hydrochloric acid and evaporating the filtrate. The residue was recrystallized from alcohol-ether.

0·2275 grms. gave 0·2219 AgCl

	Calculated for $C_6H_{10}N_2HCl$	*Found.*
Cl	24·38	24·13

The free base was liberated with sodium carbonate and extracted with ether. Recrystallized from a mixture of ether and ligroin, it forms small white needles which have a bitter taste and melt at 130 or 131°.

ON THE COMPOUND $C_{21}Cl_{26}$.

By EDGAR F. SMITH and HARRY F. KELLER.

[*Read at the Stated Meeting of the Chemical Section, March 19, 1889.*]

In 1876,† one of us (S.) described a compound, containing only carbon and chlorine. It was obtained by the exhaustive chlorination of toluene exposed to sunlight, first at the boiling temperature and then in the cold. Several analyses of the purified product showed the presence of 21·40 per cent. carbon and 78·6 per cent. chlorine. The only solvent employed at the time was chloroform, and from such a solution crystals, measuring one-half inch in length and one-fourth inch in breadth, were obtained. The forms were apparently orthorhombic. The melting point, taken after each of a series of re-crystallizations, remained constant at 152°–153° C. To this rather interesting derivative the improbable formula $C_{21}Cl_{26}$ was ascribed. Nascent

* *Ber.* **21,** 1411.

† *Dissertation.* Goettingen, 1876; *Jahresbericht,* 1877, p. 421; *Am. Phil. Soc.*, **17,** p. 29.

hydrogen acted with difficulty upon it. After an exposure of two months to the influence of zinc and sulphuric acid, it was scarcely changed, inasmuch as an analysis of the product gave 21·69 per cent. carbon, 77·76 per cent chlorine and one per cent. hydrogen.

Nothing further was done with the compound until about five years later, when a portion of it was treated in a sealed tube with an excess of aniline (*Am. Chem. Jour.*, vol. 1, p. 150). By this treatment a base was formed, melting at 230° C. Its hydrochloric acid salt was analyzed.

Crystals of the original compound, in its purest condition, were preserved for twelve years without undergoing any visible alteration, and it was but natural that we should be surprised, on fusing some of this same material, to find it melting at 101° C. This melting point remained constant, even after re-crystallization from pure chloroform. On heating a portion of the substance in a test tube, we observed that hydrochloric acid gas was evolved. A combustion gave 22·8 per cent. carbon and 2·2 per cent. hydrogen. A vapor density determination was carried out, but as we had evidence of decomposition, we place no reliance on the result. Every possible precaution was observed in the combustion, in order that we might arrive at the true hydrogen percentage, and that given above would indicate but slight change from the original constitution. Work is now being prosecuted, with a view of obtaining the carbon chloride, when it is proposed to pay especial attention to the solution of its molecular formula and to the study of some of its derivatives. We, therefore, request those who may have entertained the idea of investigating this compound to postpone their work, and leave the field to us at least for a few months.

University of Pennsylvania,
Philadelphia, March 15, 1889.

OXIDATIONS BY MEANS OF THE ELECTRIC CURRENT.

By EDGAR F. SMITH.

[*Read at the Stated Meeting of the Chemical Section, March 19, 1889.*]

In using the electric current for the determination and separation of metals, it occurred to me that its oxidizing power might be utilized to convert sulphur and other elements into higher oxides, thus bringing them into forms in which they could be readily determined. To test this I undertook the oxidation of the sulphur in chalcopyrite after the following manner: About ten grammes of solid potassium hydroxide were placed in a small nickel crucible, and carefully heated over a Bunsen burner until the water was expelled, when the flame was reduced, so that its heat was just sufficient to retain the alkali in liquid form. The crucible was put in connection with the positive pole of a battery, and the powdered mineral placed upon the alkali. A heavy platinum wire, from the negative pole, extended just under the surface of the fused mass, and when the current was passed, a lively action ensued, accompanied with considerable spattering. Loss was prevented by placing a perforated watch crystal over the crucible. When the action had continued for ten minutes the connection was broken, the crucible and its contents allowed to cool, placed in a beaker, covered with water and warmed upon an iron plate. On filtering off the insoluble oxides, the filtrate was blue in color, due to a little copper. The liquid was acidulated with hydrochloric acid, and care taken to detect any hydrogen sulphide or sulphur dioxide, which are always present, when the oxidation of the sulphur is incomplete. In this particular case all the sulphur was changed to sulphuric acid, and removed as barium sulphate. When ignited the latter presented a perfectly white appearance, showing not the slightest trace of iron.

Having succeeded so well with the first portion I weighed

off ·1734 gramme chalcopyrite, subjected it to a like treatment, and obtained ·4086 gramme $BaSO_4$ = ·0561 gramme S or 32·35 per cent. S. One of my students oxidized another portion (·5 gramme) of the same material with nitric acid and potassium chlorate, and obtained 32·54 per cent. sulphur.

The current used above registered one ampère (10·45 cc. H-O gas) per minute as it passed through the fused alkali. The solution containing the potassium sulphate contained no iron. A little copper was present in it. The residue of oxides (Fe_2O_3, CuO, etc.) should dissolve readily and completely in warm hydrochloric acid. There may, however be a residual mass, red in color, but this can be disregarded, as it is only metallic copper. In some of the oxidations the wire attached to the negative pole was coated red by copper, or with a black deposit of metallic iron. The idea suggested itself to me that, as the metal was depositing as such, it might possibly inclose some mineral, as yet unacted upon, and thus withdraw it from the field of oxidation. I therefore invariably, in every determination, reversed the current for a few minutes before its final interruption. This seems to have been unnecessary with chalcopyrite, but was required with some other minerals with which similar experiments were tried.

With a chalcopyrite, different from that analyzed before, the following percentages of sulphur were obtained :—

(1) 29·9 per cent S—(2) 30·11 per cent S—(3) 29·7 per cent S.

The quantity of mineral used was in (1) ·1528 gramme, in (2) ·1445 gramme and in (3) ·1082 gramme. About 10 grammes of potassium hydroxide were used in each determination. The current was one ampère, acting for a period of ten minutes. In working with a quantity of mineral varying from ·2 — ·3 gramme, the quantity of alkali should be doubled.

This method affords a rapid oxidation of sulphur to sulphuric acid, so that the inconveniences arising from the slow, time-consuming method with nitric acid and potassium chlorate, or that with nitric acid alone, can be avoided, where a current of the strength indicated above can be obtained.

Iron salts also are removed. I have endeavored to oxidize the sulphur of pyrite by this means, but thus far the experiments have been fruitless. I have not obtained more than half of the sulphur in the form of sulphate. Even when the current acted for thirty minutes, the result was no better. The cause of this singular behavior appears to be due to the presence of the iron. I expect, however, to so modify the experiment in this case that pyrite may yet be as easily oxidized as chalcopyrite.

As time permits, this mode of oxidation will be extended to other natural sulphides and to compounds containing sulphur.

My experiments in oxidizing with the current really began with chromite. It was treated the same as the chalcopyrite. Twice I obtained a little over fifty-three per cent. Cr_2O_3 from a specimen of this mineral, which by an older method gave fifty-four per cent. Cr_2O_3. At present I am not prepared to say anything more in regard to this mineral. Some difficulties have appeared which require solution before entering into details.

Nickel crucibles as well as iron have been used in this work, and with chromite an old platinum vessel was made to do service. The crucibles were one and one-fourth inches in height, and one and three-eighths inches wide; the most convenient form would be that measuring two inches in length, and one and one-half inches in width.

In closing I must extend my sincere thanks to Mr. D. L. Wallace, of this laboratory, for his kind assistance, without which it would have been impossible for me to carry out these experiments at this time.

University of Pennsylvania,
Philadelphia, March 19, 1889.

DISCUSSION.

Mr. Pemberton.—The application of the electric current as an oxidizing agent in chemical analysis is certainly most interesting. So far as the particular application to the analysis of pyrite is concerned, the process would be open

to the objection brought forward by Dr. Lunge to other methods of analyzing by alkaline fusion. Sulphur, present in combination (as in galenite or barite), would be reckoned available for sulphuric acid manufacture. This, however, relates to only one use of the process and is of minor importance. The principle involved is of wide application, and is a new and interesting departure in chemical analysis.

The TESTING of LOGWOOD EXTRACTS.

By T. Chalkley Palmer.

[*Read at the Stated Meeting of the Chemical Section,* Franklin Institute, *March 19, 1889.*]

The continued paper of Dr. Bruehl, now appearing in the *Textile Colorist*, on "Dyewood Extracts, etc.," while of great importance and generally very practical, contains some statements that may be challenged. This is noticeably the case when the author discusses Trimble's method of estimating the tinctorial value of logwood extracts. The description of this method, given on page 5 of the January issue, is in outline correct, but some particulars of an essential nature are not given, and the capabilities of the process are certainly misapprehended.

In order to operate successfully with this test, the following conditions must be observed. The bluestone or copper-sulphate solution, as well as the solution of extract, must be made with distilled water. The water used for dilution in the graduated cylinders, if pure distilled water, will give a reddish-purple color, quickly fading, and useless for a standard of comparison, even during ten minutes. If river or hydrant water is used, the precipitate forms into flocks immediately, and settles to the bottom of the cylinder, being likewise useless. It has been found, in practice, that the water for dilution should be three-fourths distilled water and one-fourth hydrant water. The explanation of this necessity for a certain amount of ordinary water is not, so far, at all clear; but probably a trace of ammonia, or still

more a trace of lime, is necessary to the production of the blue, finely divided lake of logwood and copper oxide. The quantity of the blue compound is, however, so minute that the slightest excess of this agent, be it what it may, produces results akin to over-oxidation.

It would, of course, be more scientific to take pure distilled water, and add enough of the needed reagent, whatever it may be, to produce the result; but the nature of this reagent not being known, and a mixture of water, as given above, producing good results, I have contented myself with this process. It only needs to be further pointed out, that as natural waters vary, varying proportions may have to be used in different places. The above proportions are for Schuylkill water.

In comparing two cylinders by this process, instead of looking at the two from above, as stated by Dr. Bruehl, it is necessary to look at them from the side; in fact, in a direction at right angles to the length of the cylinders. It is a good plan to cut off the view of the meniscus with a piece of paper or with the hand, thus leaving visible for comparison two bands of color, not complicated with any inequalities. If one looks into the tops of the cylinders, and if he has in one a standard diluted to 100 cc., and beside it an adulterated extract diluted to 50 cc., he is then comparing two columns of color, of equal richness, to be sure, but of which one is twice as deep as the other. It is very evident that this would lead to a serious error. If, on the other hand, he compares these two cylinders by a side view, he is looking through two columns of equal thickness. By this method of procedure he can get results accurate within two per cent. The description of the method has been already given pretty fully elsewhere, and though it may appear complex, is really very expeditious.

Now, in regard to the conclusion of Dr. Bruehl, that tannin-bearing matters have a disturbing effect on this reaction and that wrong values will consequently be obtained for extracts adulterated with hemlock, chestnut, etc., it is to be said that this is altogether erroneous. After a rather extensive experience in using this method, I have

perceived very clearly that it constitutes a laboratory assay rather than a dye-house test; that is, it shows more concerning the purity and the mode of manufacture of an extract of logwood than it does of its practical and effective value in the dye-house. Let me make this clear, and in doing so, it will be perceived that what the method lacks in one respect it gains in another.

Everybody knows that hemlock, chestnut, and still more cutch and sumac, are not absolute and unqualified adulterants when considered from the dyer's point of view. Most warp and other cotton-dyers habitually add cutch and hemlock to their dye-baths, either knowingly and avowedly or unknowingly under various fancy names. The *rôle* of these materials is two fold; they act as real coloring matters, producing colored lakes with the metallic salts used in dyeing, and they serve as "fasteners" or accessory mordants, aiding the ultimate color to withstand washing operations that follow dyeing. This is very ancient history. Consequently, it is far from surprising that any one who has not used Trimble's method should suppose that an equivalent result would be obtained here; that the tannins present in the extracts in question would help to form colored lakes; but it is difficult for the writer of these lines to understand how anyone can think so who has done more than meditate on the subject.

The facts in the case are these. If you weigh out three equal quantities of a given extract of logwood, and if you add to one of these an equal weight of glucose, and to another an equal weight of hemlock extract, and test the three against each other, you will get, using the pure extract for standard at 100 cc., for the one mixed with glucose, 50 cc., and for the one mixed with hemlock, almost exactly the same, but possibly 51 cc. or 52 cc. It is evident from this, that any lake produced by the union of the hemlock tannin and the copper oxide is, under the peculiar conditions of this test, colorless or nearly so. Why this should be so here, and not so under the conditions that obtain in the dye-house, it is not easy to explain, but there is no room for dispute concerning the facts.

The following results will bear out this statement of the case, being selected from many others obtained by this method on account of their bearing on the point at issue.

	Description of Extract.	Observed Dilution.	Theoretical Dilution.
		cc.	*cc.*
1	Extract logwood, 100 per cent. (Standard), ...	100·0	. . .
2	" " 85 " : Extract hemlock, 15 per cent.,	86·0	85·0
3	" " 80 " : " " 20 "	79·0	80·0
4	" " 75 " : Glucose, 25 "	75·0	75·0
5	" " 70 " : " 30 "	69·5	70·0
6	" " 66·6 " : Extract chestnut, 33·3 "	65·5	66·6
7	" " 65 " : Cutch, 25 per cent.; glucose, 10 per cent., ...	64·0	65·0
8	" " 50 " : Molasses, 50 per cent., ...	48·0	50·0
9	" " 33·3 " : " 66·6 "	33·0	33·3

It is evident that we have in this method the nearest approach to a scientific assay of logwood so far devised. By means of it we arrive at the absolute amount (roundly speaking) of logwood extract in any given sample, let the adulterant be any one or two of the substances mentioned in the above table. No doubt many things might be added to an extract of logwood that would interfere with this test, but none of the ordinary adulterants appear to do so.

Finally, the method appears capable of extension in certain directions, whereby its scientific value may be increased very greatly. If this extension proves practicable, further communication will be made concerning it.

ABSTRACTS.

On the Volumetric Determination of Sulphur by Means of Baric Chloride. C. and J. J. Beringer (*Chemical News*, **59**, 41) find this method satisfactory, if acetic acid (10 cc.) and sodium acetate (10 grammes) be added to the solution of the sulphate. The presence of free mineral acids, or of nitrates and chlorides is not objectionable, provided enough sodium acetate be added to convert all into sodium salts. L. B. H.

Commercial Production of Oxygen.—At the Stated Meeting of the Chemical Section, held March 19th, Prof. R. L. Chase made the following remarks on the commercial production of oxygen: In the *Journal of the Society of Chemical Industry*, of February 28th, there is an interesting article on "Some Industrial Applications of Oxygen." It is claimed that the gas can be manufactured in London at a cost of not over 7*s.* 6*d.* per 1,000 cubic feet.

In bleaching with chloride of lime, it was found that the addition of oxygen not only accelerated the bleaching process, but also reduced the amount of bleach necessary. Some laboratory experiments with paper pulp showed a saving of from forty to fifty per cent in the amount of bleach necessary. A practical experiment in the large way, and carried out under somewhat disadvantageous conditions, showed a saving of thirty per cent. in bleach.

The bleaching power of free chlorine was also very largely increased by the addition of oxygen.

In the purification of illuminating gas from sulphur compounds, it was found that by the addition of oxygen the lime purifiers alone were sufficient to remove all sulphur compounds, and that the lime could be used nearly twice as long as usual. Also that the luminosity of the gas was slightly increased instead of there being a decrease, as is the case when air is used.

For the maturing of spirits, it was found that by the addition of oxygen at a pressure of one or more atmospheres for ten days, the spirits were mellowed to an amount equal to that produced by three to five years' ageing. The amount of fusel oil was also largely reduced.

Researches on Silicium and Boron.—Ludwig Gattermann, *Berichte*, **22**, 186.—The author prepares silicium by heating together powdered magnesium and powdered quartz.

$$SiO_2 + 2\ Mg = Si + 2\ MgO$$

The various silicium preparations can be made from the grayish-black reaction product. If it be desired to prepare crystallized silicium, the crude silicium is heated in a luted crucible with zinc, care being taken that the temperature remains below the boiling point of the latter. By treating the fused mass with hydrochloric acid the zinc is dissolved, and steel-blue needles of silicium are obtained.

Boron may be similarly obtained by heating borax with powdered magnesium. After washing with water and then with hydrochloric acid, the residual brownish-gray powder consists mostly of boron, which may be obtained beautifully crystallized by fusion with aluminium. S. C. H.

Contributions to the Knowledge of the Sugar Group. E. Fischer and J. Tafel. *Berichte*, **22**, 97 (From the *Zeit. f. ang. Chemie*).—The authors have prepared *a*-acrose, the first synthetic representative of the group of sugars belonging to the hexan series. *a*-acrose ferments under the influence of yeast and gives all the characteristic reactions of the natural sugars, dextrose, lævulose and galactose. It does not, however, affect polarized light. It would seem probable that *a*-acrose contains a normal carbon chain formed by the condensation of two molecules of glycerin aldehyde. This synthesis is the first successful step towards the artificial preparation of the more important sugars. The authors are endeavoring to obtain an optically active sugar from *a*-acrose. S. C. H.

On Some New Tests for Tannic and Gallic Acids. By S. G. Rawson (*Chemical News*, **59**, 52).—If to a solution of tannic acid, containing one part

in 20,000 parts of water, a mixture of ammonium hydroxide and ammonium chloride be so added that the solutions do not mix, a white precipitate will be formed at the surface of contact. One part in 50,000 parts of water may be detected, if great care be taken. Gallic acid yields no precipitate under like conditions, but at the surface of contact a greenish ring may be observed. This coloration may be seen in solutions containing one part in 100,000 parts of water. L. B. H.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, April 16, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, April 16, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Dr. H. W. Jayne, Dr. Wm. H. Wahl, Dr. E. F. Smith, Dr. S. C. Hooker, Dr. H. F. Keller, Dr. D. K. Tuttle, Prof. Henry Trimble, Prof. R. L. Chase, Prof. N. Wiley Thomas, Messrs. T. C. Palmer, Reuben Haines, J. H. Eastwick, W. L. Rowland, W. W. McFarlane, W. H. Bower, F. Lynwood Garrison, Lee K. Frankel, A. W. Allen, Dr. Wm. C. Day and three visitors.

The Treasurer made a brief report, stating the present condition of the finances of the Section.

The following gentlemen were nominated for membership in the Section: Dr. L. I. Morris, 2505 Oxford Street, Philadelphia; Dr. Persifor Frazer, Drexel Building, Philadelphia; Mr. Fred. E. Ives, corner of Ninth and Filbert Streets, Philadelphia; Mr. Theodore D. Rand, No. 17 South Third Street, Philadelphia.

The President called attention to the contradictory character of two of the by-laws and recommended correction; he also recommended that one member instead of two, as at present required, be sufficient to nominate a candidate for membership.

The resignation of Dr. Isaac Norris, of 1424 Walnut Street, Philadelphia, was accepted.

The President called the attention of the Section to the fact that copies of the papers read at the last meeting had been sent as advance sheets by the Secretary to various chemical journals in the United States and abroad.

Dr. Wahl recommended that the Section continue subscription to Fittica's *Jahresbericht* recently purchased by the INSTITUTE; on motion it was unanimously voted to adopt this suggestion.

Upon the recommendation of Dr. Jayne it was decided to consider Mr. Pedro G. Salom as a member of the Section from date.

Dr. S. C. Hooker then read a very interesting paper, in which he gave the results thus far obtained in a series of sanitary analyses of the hydrant water supply of Philadelphia. These analyses include determinations of chlorine of free and albumenoid ammonia by the Wanklyn process and nitrogen in nitrates, according to the carbazol method devised by him. These analyses are to be systematically conducted at regular intervals in the future, and the results are to be embodied in future papers to be published in the JOURNAL OF THE INSTITUTE.

This paper called forth a very active and interesting discussion, which was participated in by many of the members present.

Mr. Haines suggested that in the investigation of the Philadelphia water supply, proposed by Dr. Hooker, special attention be directed to those districts which are affected with typhoid fever. In Germantown, in the Twenty-second Ward, typhoid fever has been unusually prevalent for more than a year past, but during the last three months it has increased to such an extent as to produce a general feeling of alarm and to call for a special investigation by the Board of Health. Unfortunately this investigation does not appear to have been as thorough and extended as the case demanded. It is believed that there have been in Germantown a larger number of cases of typhoid than in any other section of the city, except, perhaps, the district of Kensington, where this disease has prevailed for many years. By very many residents the disease is attributed to the Schuylkill water, which is supplied to Germantown from Flat Rock Dam, the uppermost of the pumping stations, by the Philadelphia Water Department. Prof. A. R. Leeds, of Stevens Institute, Hoboken, N. J., has stated in positive terms that the Schuylkill water has been the cause of typhoid fever in some cases. Very many residents of Germantown will not drink the river water unless it is boiled and filtered. There is, in consequence, a disposition to resort to well water instead of the river supply, a proceeding which is far more dangerous, for a large proportion of these wells, which are quite numerous, are undoubtedly contaminated with sewage.

A prominent physician, long a resident of Germantown, and who has had many of these typhoid cases, believes, on the other hand, that the disease cannot be attributed to the Schuylkill water.

Mr. Haines alluded to other causes to which the typhoid might be attributed, among which was the prevailing unsatisfactory condition of house drainage, especially in the older dwellings in Germantown, very many of which have not been arranged in accordance with the recent regulations of the Board of Health, not being properly trapped, and having no ventilating pipe to the soil pipe. Some of the houses built during the past few years are also believed to be in an unsafe sanitary condition, in consequence of improper or imperfect plumbing fixtures. The probability of a contaminated and adulterated milk supply being the cause of typhoid fever, was suggested by Dr. Tuttle.

Mr. Haines also alluded to the fact that Dr. Thos. M. Drown, of the Massachusetts Institute of Technology, has recently applied the Kjeldahl process for organic nitrogen to the determination of organic matter in water. The

result appears to warrant the belief that the process will be an important adjunct in water analysis.

Mr. Rowland suggested the determination of suspended matter as advisable.

In regard to the Kensington district Dr. Wahl referred to the extensive use of well water as the probable cause of much sickness.

Dr. Tuttle remarked on the advisability of analyzing the water of suspected wells.

The President called attention to a number of cases of typhoid fever which occurred in one family, and which were clearly traceable to contaminated well water and unsanitary conditions in the dwelling-house.

Dr. Samuel C. Hooker read a paper "On the Occurrence of Lapachic Acid in Bethabarra Wood," giving the results of an investigation undertaken in conjunction with Dr. Wm. H. Greene. The authors have unquestionably established the identity of the yellow principle of the Bethabarra wood with lapachic acid. A number of beautiful specimens were exhibited, both of the acid and of compounds prepared from it. One of the most interesting of these, lapachone, will be made the subject of further study, as the constitution which has been assigned to it is not in accordance with many new reactions observed. The results so far obtained point very strongly to the conclusion that lapachone is a derivative of naphto-furfuran and has the formula

$$C_{10}H_4 \left\{ \begin{matrix} O_2 \\ CH_2 \\ O \end{matrix} \right\} \diagdown\!\diagup CH,C_2H_7$$

The opinion was also expressed that the compound prepared by Paternò, and considered by him to be brom-lapachic acid is in reality brom-lapachone having the formula

$$C_{10}H_4 \left\{ \begin{matrix} O_2 \\ CH\,(Br) \\ O \end{matrix} \right\} \diagdown\!\diagup CH,C_2H_7$$

Dr. Smith and Mr. Frankel presented a paper on the electrolytic separation of mercury and copper, which was submitted for printing and distribution among the members, and was referred for publication.

Dr. Smith also stated that in the electrolysis of nickel and cobalt, in a solution containing potassium cyanide in excess, cobalt does not separate out, but whether these metals can be separated by this means remains to be seen.

Dr. Wahl showed some specimens of decorated glass in which the ornamentation was the result of coating a colored or flashed glass on one side with glue or gelatine, and then drying this in a current of air; the gelatine in drying contracts with sufficient force to tear away portions of the surface of the glass, thus producing striking and beautiful effects.

Adjourned.

WM. C. DAY, *Secretary.*

On the Occurrence of Lapachic Acid in Bethabarra Wood.

By Wm. H. Greene and Samuel C. Hooker.

[*Read at the Meeting of the Chemical Section, April 16, 1889.*]

A few weeks ago we were asked by Mr. A. B. Shipley, of this city, a large importer of Bethabarra wood, to investigate the properties of a yellow substance with which the pores of the wood appear to be filled. So far as we know, the wood is used in this country for the manufacture of bows and fishing-rods only, for which purpose it is admirably adapted, on account of its great tenacity and remarkable elasticity.

We have been able to learn nothing of the botanical nature of the tree yielding the Bethabarra wood, which is said to be brought from the West Coast of Africa, but we believe that we may venture the opinion that it is a species of Lapacho. The latter is one of the finest ornaments of the sub-tropical hills and plains of South America. Its far spreading branches are in the spring covered with masses of flowers, red or yellow, according to the variety, so dense that the rays of the sun cannot penetrate them. Its wood is very hard, susceptible of a fine polish, and resists indefinitely the action of moisture.

The considerable cost of the wood made it desirable that, if possible, some use should be found for the refuse.

A few preliminary experiments with the extracted substance showed us that it contained a compound of much scientific interest, and for this reason we felt justified in undertaking the research, independently of any pecuniary result with which we were not concerned.

On referring to the literature of the subject, we found a paper entitled "Preliminary Notice of a New Vegetable Coloring Matter," published by Samuel P. Sadtler and William L. Rowland in December, 1880,* concerning the principle of the Bethabarra wood. Aside from analyses,

* *Amer. Chem. Jour.*, **3**, 22.

this paper throws but little light on the constitution and properties of the substance, dealing mainly with a comparison of the color reactions of the Bethabarra principle with crysophanic acid, santalin, hæmatoxylin and brasilin. The analyses of the authors left them undecided between the formulæ $C_{28}H_{29}O_5$ and $C_{22}H_{23}O_4$, and they conclude their paper with a suggestion that a close relationship exists between the Bethabarra principle and crysophanic acid and hæmatoxylin.

The Bethabarra wood used in our investigation was mainly in the form of sawdust. This was extracted in quantities of about five kilogrammes at a time by percolation with a cold one per cent. solution of crystallized sodium carbonate; the solution was allowed to remain in contact with the wood for several hours, and then drawn off, and the operation was repeated three or four times until the intensity of the deep red color of the extract was much diminished. The liquid was then treated with an excess of hydrochloric acid, and the precipitate allowed to settle, the excess of acid being necessary to insure the rapid separation of the precipitate. The clear liquid was then siphoned off, and the precipitate collected on a filter and dried.

This extract consists of the crystalline principle of the wood, accompanied by a resin, and as both are readily soluble in alcohol, this is not a desirable agent for the first crystallization as recommended by Sadtler and Rowland. On the other hand, we found the resin to be practically insoluble in ether, which freely dissolves the crystalline substance. The dry substance was broken up and shaken with ether in a closed flask; the addition of a few drops of water causes the resin to agglomerate and adhere to the walls of the flask; the ethereal solution could then be poured off without filtration. This operation was repeated with fresh ether; the ether distilled off, and the crystalline mass obtained was thrown on a filter and washed with a little alcohol at the pump. In this way the substance was obtained in a nearly pure condition, one recrystallization from alcohol yielding an absolutely pure product equal in quantity to at least 0·6 per cent. of the wood employed.

After a brief examination of our substance, we were struck by the remarkable similarity of its properties with those of taiguic acid,* which will be found described in Gmelin's Hand-Book, xvi, 521, and which has been shown by Paternò† to be identical with the greenhartin of Stein‡ and with the lapachic acid of Siewert.§ Under the latter name, this substance has been the subject of an admirable research by E. Paternò,‖ who from a series of concordant analyses deduced the formula $C^{15}H^{14}O^3$, and was able to assign to it with great probability the constitution of an amylene-oxynaphthaquinone.

$$C_{10}H_4 \begin{cases} CH = CH - CH\,(CH_3)_2 \\ O \\ OH \end{cases}$$

A close examination of the Bethabarra principle established its complete and unquestionable identity with lapachic acid. Its fusing point is 139°·5–140°·5; that of lapachic acid, as given by Paternò, is 138°.

We have prepared a number of characteristic salts. That of ammonia is unstable, losing ammonia with great readiness; a dilute solution of this salt deposits crystals of the acid when evaporated, as observed by Paternò with the ammonium compound of lapachic acid.

The silver salt is obtained as a bright red amorphous powder; on analysis we obtained the following figures:—

I. 0·2594 gr. gave 0·0795 gr. silver.
II. 0·2674 " " 0·0830 " "

	Found.		*Calculated for* $C^{15}H^{13}O^3Ag$.
	I.	*II.*	
Ag	30·65 per cent.	31·04 per cent.	30·95 per cent.

Mean of analyses by Paternò, 30·87 per cent. Ag. Analyses I and II were of compounds prepared separately.

* *Comptes rendus*, **46**, 1,152.

† *Gaz. Chim. Ital.*, 1879, **9**, 505.

‡ *Jour. prak. Chemie*, **99**, 1.

§ *La République Argentine*, par R. Napp, aidé de plusieurs collaborateurs. Ouvrage écrit par ordre du Comité central Argentin pour l'Exposition de Philadelphia. Buenos Ayres, 1876.

‖ *Gaz. Chim. Ital.*, **12**, 337–392.

By reducing agents the Bethabarra principle is converted with great facility into a white crystalline substance, which rapidly absorbs oxygen from the air, being reconverted into the original compound. This also characterizes lapachic acid.

By the action of concentrated sulphuric acid we have obtained a beautiful orange-red, quinone-like, crystalline substance, fusible at 155°–156° and identical with lapachone.* Concentrated nitric acid in the cold gives rise to the same substance, as shown by Paternò.

As the unexpectedly rapid result of our research has left us sufficient material to extend our investigations, and as the constitution assigned by Paternò to lapachone is not in accordance with some reactions which we have observed, we purpose to make this compound the subject of further study.

PHILADELPHIA, 10th April, 1889.

ON THE PRESENT CONDITION OF THE PHILADELPHIA WATER SUPPLY. FIRST MONTHLY REPORT

By SAMUEL C. HOOKER, Ph.D.

[*Read at the Stated Meeting of the Chemical Section, April 16, 1889.*]

Many considerations have induced me to undertake a systematic and frequent chemical examination of the water supplied to this city, and at the outset it would seem desirable that I should briefly enumerate some of the principal reasons for the investigation, and mention some of the beneficial results which it is to be hoped may arise from it. In approaching this question of the water supply of Philadelphia, which has given rise to so much discussion and difference of opinion, I desire it to be understood that I am primarily seeking for information, and that I wish to ascertain as nearly as possible the condition of the water at *all* times. We hear occasionally when the water is bad, but we

* Paternò, *loc. cit.*, 372.

do not hear when it is good. We should be acquainted with the good as well as with the bad aspect of the case, and deal with the question in a fair and unprejudiced manner. With the advantages offered by the large subsiding basin in the East Park, and with increased care in the prevention of the access of foul matter to the Schuylkill River, we should ask ourselves whether the condition of the water has so improved as to render it generally good, and to leave the times at which it may be seriously open to suspicion so few and far between as to make them of comparatively small importance. This is a question which can only be answered by a thorough and systematic examination such as I have commenced. Isolated analyses of samples purposely taken at times when everything conspires to make the water unusually bad, are of comparatively small value. Indeed, the information they give is such as to be positively misleading and to urge the belief that the water is at all times far worse than is really the case.

At the time my investigations were commenced the water was not systematically analyzed at regular and frequent intervals, and such analyses as were fitfully made, were not accessible to the public. The last published reports of the Water Department and also of the Health Department do not contain a single analysis, a fact which speaks more strongly than any other for the needs of such work as I have undertaken. The very unfavorable opinion to which—rightly or wrongly—some of the best known experts who have examined into the matter have come, regarding the condition of the Schuylkill River in the past, renders it highly desirable that the water supplied to the city should at all times be under chemical supervision. The interests of the public demand it. In the case of a river which is liable to pollution, it is obvious that circumstances may arise to make the water at times more than ordinarily dangerous. By frequent chemical examinations such a condition of the water would be detected at once, the public could be warned of it, and steps taken to find and remove, or at least mitigate the cause of the trouble. It is, therefore, extremely desirable that the water should be very frequently

analyzed, both for the information and protection of the public.

Aside from throwing some light on the question of wholesomeness, it is to be hoped that the present investigation may arouse public interest, with the view to pushing forward such improvements as will be instrumental in securing a *cleaner* supply.

In the face of such difference of opinion as exists regarding the wholesomeness of the Schuylkill, it is certainly satisfactory to find one point upon which all are agreed, and which does not admit of contradiction or argument. For whether the water be wholesome or unwholesome, whether it be charged with sewage or free from such contamination, whether it be loaded with or free from disease, it cannot be denied that the muddy condition of the water very frequently supplied to certain sections of the city, and at intervals to others, is a great and ever increasing disgrace to the city of Philadelphia.

The samples of water for analysis are drawn every Friday morning from six sections of the city, which have been carefully selected, so as to include all the probable variations in condition which the supply may simultaneously present at different portions of the city. This refers only to the water from the Schuylkill.

The samples are collected in the following neighborhoods:

(1) Sixteenth and Locust.
(2) Front and Bainbridge.
(3) Forty-fourth and Chestnut.
(4) Beach and Vienna.
(5) Twentieth and Columbia Avenue.
(6) 4000 Germantown Avenue.

(1) The first of these localities is usually supplied from the Spring Garden pumping station through the Corinthian Avenue basin. It may also be supplied from the Fairmount, Spring Garden and East Park reservoirs. The water at this point represents the supply of the district between Vine and South Streets.

(2) The city below South Street is fed by the Fairmount pumping station through the Fairmount reservoir. This part of the city may also be supplied in case of necessity from the Corinthian Avenue basin.

(3) The sample drawn at Forty-fourth and Chestnut is representative of the whole of West Philadelphia. The water is pumped at the Belmont Station and supplied through the Belmont reservoir.

(4) Kensington, in which Beach and Vienna is situated, formerly received its supply from the Delaware. Since the middle of September, 1888, Schuylkill water has been fed to this district. In future it is proposed to pump Delaware water only in the case of emergency.

(5) The water drawn at Twentieth and Columbia Avenue represents that of the whole of the Northwestern portion of the city. This district, which is bounded on the north by Allegheny Avenue, on the south by Vine Street, and on the east by Broad Street, is supplied by direct pumpage from the Spring Garden works.

(6) The Twenty-second and part of the Twenty-eighth Wards are supplied from the Mt. Airy reservoir, which is fed from the Roxborough Station. The water drawn at Germantown Avenue represents this district.

By thus collecting the water as actually supplied to the city instead of taking it directly from the river or the reservoirs, not only are fairer samples obtained, but the water should be at its best, having had the advantage of passing through the subsiding basins.

It is to be hoped that as improvements are made a careful study of these reports will lead to those sections of the city which are at present worst off being first considered.

Although a lengthy discussion of the methods of analysis is unnecessary, it may be well briefly to mention the processes employed.

The determinations of albumenoid and free ammonia were made in all essential particulars as recommended by Wanklyn. Duplicate analyses, occasionally made to test the accuracy of the results, gave figures so closely cor-

responding to the first determinations as to leave little to be desired.

The chlorine was estimated by the well-known volumetric process. The greatest possible care was taken with these determinations, as very slight variations appear of considerable importance. Duplicate determinations were made in every case and the mean of at least two experiments taken. The nitrates were determined by the carbazol process, devised by myself, and already described in detail to the Section.

The following table gives the results obtained:

ANALYSIS OF THE PHILADELPHIA WATER SUPPLY.

Kensington, Beach and Vienna.

Date. 1889.	*Chlorine.*	*Free Ammonia.*	*Albumenoid Ammonia.*	*Nitrogen of Nitrates.*
March 15th,	·32	·0005	·0055	·14
" 22d,	·32	·0005	·0050	·14
" 29th,	·38	·0005	·0065	·12
[April 5th,	·51	·0075	·0190	·07]
" 12th,	·34	·0005	·0070	·10
Average, omitting the sample of April 5th, as from the Delaware,	·34	·0005	·0060	·125

West Philadelphia.

March 15th,	·30	·0025	·0045	·14
" 22d,	·15	·0020	·0050	·14
" 29th,	·27	.0025	·0070	·11
April 5th,	·27	·0020	·0075	·10
" 12th,	·31	·0010	·0065	·10
Average,	·26	·0020	·0061	·118

Sixteenth and Locust.

March 15th,	·27	·0000	·0105	·14
" 22d,	·24	·0000	·0070	·14
" 29th,	·35	·0015	·0075	·12
April 5th,	·26	·0015	·0080	·11
" 12th,	·35	·0010	·0085	·10
Average,	·29	·0008	·0083	·122

Front and Bainbridge.

Date. 1889.	*Chlorine.*	*Free Ammonia.*	*Albumenoid Ammonia.*	*Nitrogen of Nitrates.*
March 15th,	Sample not forwarded.			
March 22d, ...	·32	·0005	·0075	·14
" 29th, ...	·36	·0005	·0055	·12
April 5th, ...	·28	·0010	·0070	·10
" 12th, ...	·35	·0010	·0090	·09
Average, ...	.32	·0007	·0072	·112

Twentieth and Columbia Avenue.

March 15th, ...	·30	·0000	·0070	·13
" 22d, ...	·35	·0005	·0100	·14
" 29th, ...	·37	·0020	·0085	·11
April 5th, ...	·26	·0015	·0140	·11
" 12th,	Demijohn broken in transit.			
Average, ...	·32	·0010	·0098	·122

4000 Germantown Avenue.

March 15th,	Sample not on time.			
" 22d, ...	·25	·0005	·0110	·12
" 29th, ...	·30	·0005	·0165	·11
April 5th, ...	·26	·0015	·0125	·10
" 12th,	Sample not on time.			
Average, ...	·27	·0008	·0133	·110

All the above results are expressed in parts per 100,000.

It will be apparent to any one at all familiar with the subject, that the worst feature of these analyses lies in the comparatively large amount of nitrates. Apart from this, the condition of all the samples examined from the Schuylkill—twenty-four in number—is very satisfactory, and if maintained throughout the year, would render any serious anxiety as to the wholesomeness of the supply quite unnecessary. It is certainly gratifying to find the condition of the water so uninterruptedly satisfactory during a whole month, and so much better than one could have fairly expected from the pessimistic reports which have recently from time to time been published in the newspapers. It will be understood that I am at present speaking of the

quality of the water without reference to its muddiness. With regard to this latter particular, the condition of all the water could not by any means be said to be satisfactory.

It will be observed that the sample drawn at Beach and Vienna on April 5th, was vastly inferior to the remaining samples collected at the same locality on other days, and also to the other samples collected at other points on the same date. Although I had information that Kensington was drawing its water from the Schuylkill I could not believe that this was really the case at the time that this particular sample was drawn. I consequently made a personal visit to the Kensington Water Works, on April 11th, to clear up the matter, and was gratified to find that my surmise was correct. The pump at the works was drawing water from the Delaware at that date, and had been doing so since April 3d, on account of a breakdown at the Spring Garden Station.

Pumping from the Delaware, at the Kensington Works, still continues at the present date, but the Lehigh basin, into which the water is forced, is apt to be low towards the evening, at which time the overflow from the Spring Garden basin is permitted to flow into it. Samples collected in the early morning may, therefore, consist almost entirely of Schuylkill water. This explains the good condition of the water from this district on April 12th, and its very great similarity to the samples drawn previous to April 3d.

From an examination of the table it will be observed that on the whole the quality of the water in each locality has been very uniform doing the past month. There is, however, a marked difference in some respects in the water from the different localities. For instance, the free ammonia is almost constantly higher in West Philadelphia than in other portions of the city, and similarly the albumenoid ammonia is higher in Germantown than elsewhere. Should these differences be maintained, they will be fully considered in detail in subsequent reports.

My observations so far show that the albumenoid ammonia is greater in the turbid samples, even after filtration through paper, than in the clearer ones, or in other words that the

albumenoid ammonia is in some degree proportional to the turbidity.

This is well shown in the following table:

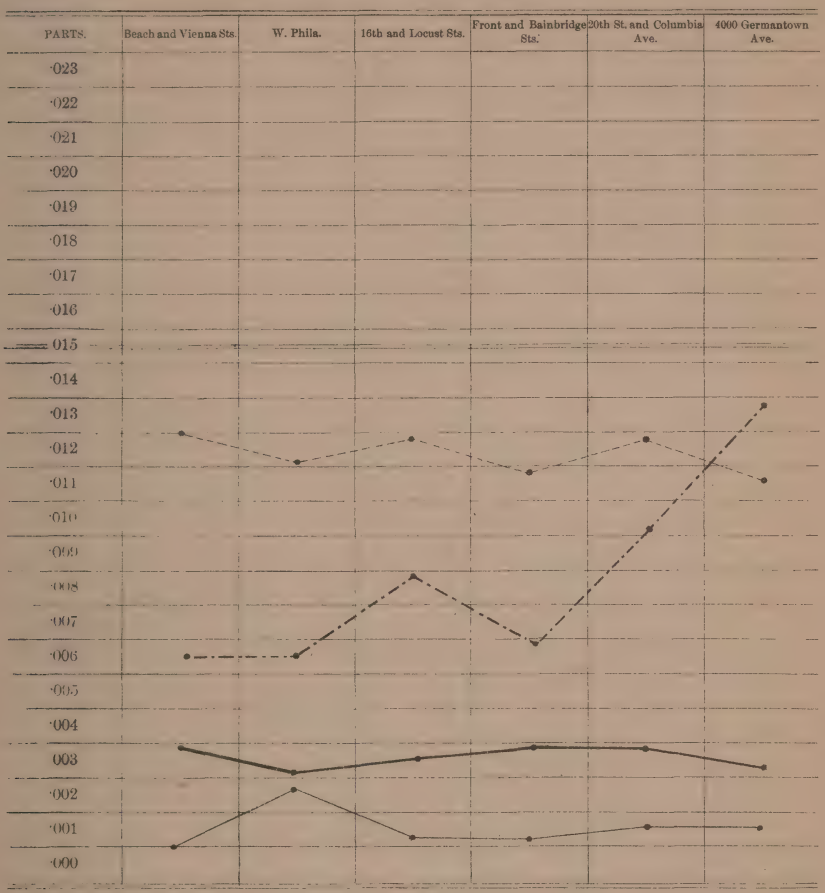
Average order of turbidity for the month. The water from the first locality being the best, i. e., the brightest.	*Average of albumenoid ammonia for the same period.*
1. Kensington,	·0060
2. West Philadelphia,	·0061
3. Sixteenth and Locust,	·0083
4. Front and Bainbridge,	·0072
5. Columbia Avenue,	·0098
6. Germantown,	·0133

The full meaning of this, which has, I believe, considerable bearing on the quality of the Germantown water as compared with that of other localities, will be considered in a subsequent report when the data collected have become somewhat larger.

As it is intended that the results of these analyses may clearly and readily be understood by those who are not chemists, a diagram is appended, which it is believed will be made thoroughly intelligible to all by the aid of the explanatory notes accompanying it.

DIAGRAM SHOWING THE AVERAGE RELATIVE CONDITION OF THE WATER SUPPLY AT DIFFERENT POINTS OF THE CITY. March 15 to April 12, 1889.

(CONSTRUCTED FROM 24 ANALYSES.)



EXPLANATORY NOTES:

Nitrogen of Nitrates in parts per 10,000.
Representing, when in excess, animal matter, which by natural processes of purification has been rendered harmless.

Albuminoid Ammonia in parts per 100,000.
Representing, when in excess, nitrogenous organic matter of the most dangerous type.

Chlorine in parts per 1,000.
Representing, when in excess, present or past sewage contamination.

Free Ammonia in parts per 100,000.
Representing, when in excess, decaying organic matter.

Provided that the two lower curves do not vary much in height from those given, the condition of the water may be regarded as satisfactory, so long as the two upper curves remain below the double line through ·015.

It will be understood that the smaller the quantity of the substances indicated by the above curves, the more satisfactory the condition of the water. In other words, the water is most satisfactory with regard to each particular substance, at the lowest point of each curve.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, May 21, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, May 21, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Mr. Chas. Bullock, Prof. R. L. Chase, Dr. W. C. Day, Mr. Lee K. Frankel, Dr. Wm. H. Greene, Mr. Reuben Haines, Dr. L. B. Hall, Dr. S. C. Hooker. Mr. Fred. E. Ives, Dr. H. W. Jayne, Dr. H. F. Keller, Mr. T. C. Palmer, Mr. W. L. Rowland, Prof. S. P. Sadtler, Dr. E. F. Smith, Prof. Henry Trimble, Dr. Wm. H. Wahl.

Dr. Greene called the attention of the Section to the fact that efforts are now being made by the American Association for the Advancement of Science to form a National Chemical Society, with headquarters in Washington, and which shall hold regular annual meetings. He further stated that he had been requested by a member of the American Association to bring the matter before the Chemical Section of the INSTITUTE, with the object of securing the nomination of delegates to represent the Section in the matter at a meeting to be held at the same time and place with that of the American Association, to be held during the coming summer.

After some discussion by the President and Drs. Hall, Wahl and Greene, on motion of Dr. Greene, it was voted that the President appoint a committee to investigate the matter more fully, and report to the Section at its next meeting. The President appointed Drs. Greene, Hall and Wahl members of this committee.

Professor Sadtler then read a paper, "On the Presence of Paraffine in Crude Petroleum," which was referred for publication.

Mr. Charles Bullock read a paper "On the Preparation and Properties of Pure Metallic Manganese." He also exhibited two specimens of metallic manganese; one of them had been obtained by reducing chloride of manganese by means of sodium, using fluor spar alone as the flux, and the other by using chloride of sodium without fluor spar. The paper was referred for publication.

Dr. Keller followed with a paper "On Kobellite from Colorado, and the Chemical Composition of this Mineral;" also, "An Analysis of Megabasite." Some very fine specimens of the minerals were exhibited by Dr. Keller. The paper was submitted for publication.

Dr. Hooker then read his report "On the Philadelphia Water Supply" for the past month. Aside from the muddiness of the water, the report was favorable to the present condition of the supply. The report was submitted for publication.

A paper "On the Electrolytic Separation of Cadmium from Zinc," by Dr. Smith and Mr. Frankel, was next read by Dr. Smith. It was submitted for publication.

Dr. Smith also read a paper entitled, "Derivatives Obtained from Mono-Chlor-Dinitro-Phenol and Bases of the Aromatic Series."

This paper is preliminary to an investigation now going on. It was referred for publication.

Dr. Greene then followed with recent results obtained by him and Dr. Hooker in their investigation of lapachic acid and its derivatives.

Upon recommendation of the President and motion of Mr. Palmer, it was voted that the notification of members of the meetings of the Section be attended to, under the direction of Dr. Wahl, by one of the clerical force of the INSTITUTE.

Adjourned.

WM. C. DAY, *Secretary.*

A RAPID COLORIMETRIC METHOD OF DETERMINING NITRATES IN POTABLE WATERS.*

By Samuel C. Hooker, Ph.D.

[*Read at the Stated Meeting of the Chemical Section of the* Franklin Institute, *March 19, 1889.*]

In devising a process for the estimation of nitrates in the minute quantities in which they occur in natural waters, I have not been ignorant of the fact that there are already several very satisfactory ways in which this can be accurately done. I have, however, aimed at greater rapidity than has heretofore been possible.

Fully fifteen years ago Graebe and Glaser discovered carbazol, and observed that when dissolved in concentrated sulphuric acid it gave rise to an intensely green solution on the addition of nitric acid. This reaction, which up to the present time has been used only as a means of identifying carbazol, forms the basis of the process to be described. Its extraordinary delicacy renders it particularly suitable for the purposes of water analysis, and enables a quantity of nitric acid, containing as little as $\frac{6}{10,000}$ of a milligramme of N to be accurately determined. The reaction is not, however, peculiar to nitric acid; all oxidizing agents behave similarly. Graebe and Glaser enumerate chlorine, bromine, iodine, nitrous and chromic acids as giving rise to the same intensely colored solution. With the exception of nitrous acid, the substances just mentioned are almost invariably absent from natural waters, and may therefore be dismissed from further consideration. There is, however, one other oxidizing agent, namely iron in the ferric condition, which is sometimes found in very appreciable quantities, and it therefore became necessary, in studying the influence of the substances in solution upon the process, to give special attention to iron as well as to nitrous acid.

* See preliminary paper, Journal of the Franklin Institute, **127,** 16.

As the result of a number of careful experiments, the following conclusions were arrived at with regard to the application of the process:

(1) No material error will arise in the presence of nitrites in the quantities in which they usually occur.

(2) Iron (in the ferrous or ferric condition), if present in quantities greater than 0·1 parts per 100,000, must be removed.

(3) Chlorides, even when present in very small quantities, must be removed.

(4) Carbonate of lime, sulphates of lime, soda, etc., in the quantities in which they ordinarily occur, were not found to influence the determinations.

(5) The presence of easily destructible organic matter, such as albumen, lowers the result, not materially, however, unless present in large excess.

The estimation, briefly described, is made as follows:

Two cubic centimetres of the water to be examined is mixed with 4 cc. concentrated sulphuric acid; the mixture is cooled and a small quantity of carbazol, dissolved in sulphuric acid, added. If nitric acid be present, the solution will turn green on the addition of the carbazol, and the intensity of the color, by comparison with that produced by solutions of potassic nitrate of known strength, will, within certain limits, indicate the amount of the acid present.

The great majority of waters can be estimated directly without previous concentration, and only a few will need to be diluted. The limits within which the determinations may be safely made are marked by quantities of nitric acid representing ·03 and ·40 parts N per 100,000. Water containing either less or more nitric acid than indicated by these figures must be concentrated or diluted.

To test the accuracy of the process, a number of solutions were prepared, at my request, containing different quantities of potassic nitrate. In order that my judgment might not be influenced by a knowledge of the amount of nitric acid present, I was kept in ignorance of the strength of the solutions until after the estimations had been completed.

The following are the results obtained:

NITRIC ACID EXPRESSED AS N IN PARTS PER 100,000.

Present.	*Found.*	*Error.*
·127	·130	+ ·003
·078	·075	— ·003
·200	·190	— ·010
·302	·300	— ·002
·290	·290	·000

Average error, ... ·0036

NITRIC ACID PRESENT IN THE 2 CC. OF WATER OPERATED UPON EXPRESSED IN DECIMALS OF A GRAMME.

Present.	*Found.*	*Error.*
·00001143	·00001170	·00000027
·00000702	·00000675	·00000027
·00001800	·00001710	·00000090
·00002718	·00002700	·00000018
·00002610	·00002610	·00000000

Average error, ... ·000000324

The above results are not selected, but include all the determinations that have been made with solutions of unknown strength, with the object of testing the delicacy of the process. It is to be borne in mind, that potassic nitrate *only* was present. Considering the extremely minute quantities operated upon, the accuracy of the above results is very noteworthy.

The following reagents are required:

(1) Concentrated sulphuric acid.
(2) An acetic acid solution of carbazol.
(3) A sulphuric acid solution of carbazol.
(4) Standard solutions of potassic nitrate.
(5) A solution of aluminic sulphate.
(6) A standard solution of sulphate of silver.

(1) The sulphuric acid, used for all purposes in the process, should be almost entirely free from oxides of nitrogen. It may be readily tested by dissolving in it a small quantity of carbazol. If the solution be at first golden yellow or brown, the acid is sufficiently pure; if it be green or greenish, another and better sample must be taken. It is essential also that the specific gravity of the acid be fully 1·84,

and it is well to ascertain that this is really the case, as I have found several samples, obtained from sources which are generally thought reliable, to fall considerably below these figures. The acid was in fact worthless for the purpose required.

(2) The carbazol used was obtained from Kahlbaum,* of Berlin. The acetic acid solution is prepared by dissolving 0·6 gramme in about 90 cc. of 99–100 per cent. acetic acid, by the aid of gentle heat. It is allowed to cool and is then made up to 100 cc. by the further addition of acetic acid. The exact strength of this solution is of no material importance to the success of the process, and the above proportions have been selected principally because they are convenient. The solution will probably remain unchanged almost indefinitely; but I cannot speak positively in this respect, as my actual experience extends only over a period of several months. The use of this solution merely facilitates the preparation of that next described, which will not keep, and has consequently to be freshly prepared for each series of determinations.

(3) The sulphuric acid solution of carbazol is easily made in a few seconds, but it is advisable to allow it to stand from one and one-half to two hours before using. It is prepared by rapidly adding 15 cc. of sulphuric acid to 1 cc. of the above described acetic-acid solution. This quantity usually suffices in my hands for from two to three nitrate estimations. When freshly prepared it is golden yellow or brown; it changes gradually, however, and in the course of one and one-half or two hours it becomes olive-green. I am not able to say positively to what this change is due, but it seems probable that traces of oxidizing agents occur in the sulphuric and acetic acids, and that these, although not present in sufficient quantity to act immediately, gradually bring about the reaction described. The greenish color does not interfere with the process, as might at first be supposed; on the contrary, I have observed that the solution is not sensitive to small quantities of nitric acid until

* Kahlbaum's carbazol may be obtained from James W. Queen & Co., Philadelphia.

it has undergone the change to olive-green, and it is for this reason that I have advised that it should be prepared about two hours before required for use. This solution may be thoroughly depended on for six hours after preparation. The intensities of color produced by the more concentrated solutions of nitrates after this time, gradually approach to each other and become ultimately the same.

(4) The standard solutions of potassic nitrate are very readily prepared. The solutions which are to be compared directly with the waters examined, may be prepared as required, but if many determinations are to be made with a variety of waters, it will be found best to prepare a complete series, differing from each other by ·02 parts N in 100,000. This series may include solutions containing quantities of nitrogen in 100,000 parts, represented by all the odd numbers from ·03 up to ·39. It will be found convenient to prepare them in quantities of 100 cc. at a time, from a stock solution of potassic nitrate (b), which contains ·00001 gramme N, or ·000045 HNO_3 in 1 cc. Each cubic centimetre of this solution, when diluted to 100 cc., represents ·01 N in 100,000, and consequently if it is desired to make a solution containing ·35 parts N in 100,000, 35 cc. are taken and made up to 100 cc., and so on. The solution of potassic nitrate (b) is best prepared from a stronger one (a), containing ·0001 gramme N to the cubic centimetre, or ·7214 gramme KNO_3 to the litre: 100 cc. of (a) made up to one litre, gives the solution (b). It is obvious that the series of solutions above described could be made directly from (a), but by first making (b) greater accuracy is secured.

(5) For purposes which will be presently described, a solution of aluminic sulphate is required, containing five grammes to the litre. The salt used must be free from chlorine and iron; and the solution should give no reaction when tested, as in the case of a water with carbazol.

(6) The standard solution of sulphate of silver is required for the removal of chlorine from the water to be examined. It is prepared by dissolving 4·3943 grammes of the salt in pure distilled water and making up to one litre. The sul-

phate is preferably obtained by dissolving metallic silver in pure sulphuric acid. The solution should be tested with carbazol in the same way as will be presently described for water; if perfectly pure no reaction will be obtained. As sulphate of silver is often prepared by precipitation from the nitrate, it is very apt to contain nitric acid, and consequently if the source of the salt be not known, this test should on no account be omitted.

Having described the preparation of the reagents, the method of making the determinations may now be considered more in detail. Assuming the water to be free from all substances capable of affecting the accuracy of the results, the process is carried out as follows: Two cubic centimetres of the water is carefully delivered by means of a 2 cc. pipette into the bottom of a test tube; 4 cc. of sulphuric acid is added, and the solution thoroughly mixed by the help of a glass rod. The test tube is then immersed in cold water, and when well-cooled 1 cc. of the sulphuric acid solution of carbazol is added, and the whole again mixed as before. The intensity of the color is now observed, and a little experience enables a fairly good opinion to be formed of the quantity of nitric acid present. Suppose that the water is roughly estimated to contain about ·15 parts N per 100,000, solutions of potassic nitrate, containing ·11, ·15, ·19 parts N, are selected from the series. Two cubic centimetres are taken from each and treated side by side with a fresh quantity of the water, precisely as described for the preliminary experiment, the various operations being performed as nearly simultaneously as possible with each of the samples, and under precisely similar conditions. Two or three minutes after the carbazol has been added, the intensity of the color of each is observed. If that given by the water is matched by any of the standard solutions, the estimation is at an end. Similarly, if it falls between two of these, the mean may be taken as representing the N present in cases in which great accuracy is not required. If this be done, the maximum error will be ·02 N or ·09 parts HNO_3 per 100,000. If greater exactness be required, or it be found that the color given by the water is either darker or lighter than that given by all

the standard solutions, a new trial must be made. In such a case the water must be again tested simultaneously with the solutions with which it is to be compared. This is rendered principally necessary for the reason that the shade of the solutions to which the carbazol has been added is apt to change on standing. Hence, it is desirable that the water, and the standard potassic nitrate with which it is to be compared, should have the carbazol added at as nearly the same time as possible. When finally the color falls between that given by any two consecutive members of the standard potassic nitrate series, the estimation may be considered at an end, and the mean of these solutions taken as representing the N present. The maximum error in this case will be only ·01 N per 100,000 parts, and the mean error slightly more than ·005. This degree of accuracy is believed by the author to be quite sufficient for, if indeed it does not exceed the needs of, all ordinary cases of water analysis for sanitary purposes, for which the process was specially devised. If occasionally, however, greater accuracy is desirable, the determinations recorded in the early portion of this paper show that the average error can be reduced to ·0036 parts N per 100,000. In this case the standard solutions employed must differ from each other by ·01 parts N only. The additional accuracy gained, however, will scarcely repay for the extra time and labor required, and even in this case, as will be seen by a reference to the above determinations, the error may amount to ·01 parts N per 100,000.

In the course of a great many experiments I have observed, even when the utmost care has been taken, that two solutions, nominally containing the same amount of nitric acid, occasionally give a very slight though distinctly perceptible difference in shade when tested side by side. Whatever may be their cause, such differences are extremely slight, and if proper care be taken do not materially affect the value of the process.

I cannot too strongly insist upon the necessity of scrupulous cleanliness at all stages of the analysis. The quantity of water operated upon is so small, that if the greatest care be not exercised throughout, sources of con-

siderable error may be readily introduced. The test tubes used in the process may be conveniently 5 x ⅝ inches in size. It is scarcely necessary to add that they should always be dry when used, and rinsed out carefully with distilled water when put aside.

In comparing the color given by a water with that produced by standard potassic nitrate, it is necessary only to examine the solutions *through* the tubes; differences in shade, which can only be detected by looking through the length of the columns of liquid, may be disregarded. It is well to use the same 2 cc. pipette for measuring both the water and the standard potassic nitrate; the effect of any error in graduation is thus neutralized.

I have made experiments to ascertain whether the intensity of color produced is strictly proportional to the nitric acid present, with a view to render the use of a colorimeter possible and thus to avoid the time and trouble necessary to match the colors given by the waters. The result of these experiments, which were made with a Duboscq instrument, show conclusively that the changes already referred to in both tint and intensity after the addition of the carbazol, occur more rapidly with the light than with the dark solutions, and hence they are not strictly comparable.

INFLUENCE OF NITRITES.

It has been already pointed out that nitrous acid behaves similarly to nitric acid in its action on a sulphuric acid solution of carbazol. In order to estimate to what extent its influence would be felt when present in the water to be examined for nitrates, several solutions of silver nitrite were carefully prepared and estimated precisely as if they contained a nitrate.

The results obtained are given in the following table:

RESULTS EXPRESSED AS N IN 100,000 PARTS.

Present as $AgNO_2$.	*Found.*	*Error.*	*Corrected by deducting one-fifth from amount found.*
·10	·12	·02	·096
·20	·25	·05	·200
·30	·37	·07	·296

It will be observed that the error may be very nearly corrected by deducting one-fifth from the amount found. In the presence of nitrates, this correction, of course, will only be possible in cases in which the quantity of the nitrous acid present has been previously ascertained. A correction, however, would be rarely necessary.

INFLUENCE OF IRON.

Although a solution of ferrous sulphate gives no reaction with carbazol, nitrates are apt to be overestimated in the presence of iron in the ferrous condition. Ferric salts, however, acting like other oxidizing agents, are themselves able to give the characteristic green color with carbazol. I have made a number of experiments with solutions of potassic nitrate in the presence of both Fe″ and Fe‴ in varying amounts, and have ascertained that if iron be not present in quantities greater than 0·1 parts per 100,000, the error will not exceed ·01 parts in 100,000. The condition of a water with regard to iron may be ascertained sufficiently accurately in a few seconds by the help of ammonic sulphide. As this is a test which should always be made in the examination of water for sanitary purposes, no extra trouble is involved. In a case in which iron is present in large quantities, it can be easily eliminated by rendering the water slightly alkaline, evaporating to dryness, and redissolving the soluble residue in the same volume of pure distilled water, as was taken of the water under examination.

INFLUENCE OF CHLORIDES.

Chlorides form by far the most serious source of error in this process by intensifying the action of the nitric acid. If, however, nitrates be absent, chlorides give no reaction with carbazol. Were it not for the fact that the chlorine can be perfectly removed in the space of a very few minutes, the general usefulness of the method would be much restricted. In order to remove the chlorine I use the standard sulphate of silver already referred to, 1 cc. of which, when consumed by 100 cc. of water, is equivalent to one part of Cl in 100,000 parts of water. Having first determined the chlorine present, by means of a standard nitrate

of silver solution of equivalent strength, the exact quantity of sulphate of silver required is known. I proceed as follows: A flask, graduated on the neck at 100 cc. and 110 cc., is filled up to the 100 cc. mark with the water to be examined. The necessary quantity of sulphate of silver is next added and then 2 cc. of the solution of aluminic sulphate previously described; finally, the contents of the flask are brought up to the 110 cc. mark by the addition of pure distilled water. The whole is shaken up and filtered; the first portion of the filtrate, which will contain any foreign substances derived from the filter paper, is thrown away. The aluminic sulphate, by reacting with the carbonates usually present in the water, and thus giving rise to the precipitation of alumina, facilitates the removal of the precipitated chloride of silver, which otherwise, under the conditions given above, is extremely difficult to separate and may even still pass through the paper after refiltering many times. When the filtrate is perfectly bright, a portion is tested to make sure that all the chlorine is removed; the estimation is then made precisely as already described, the amount found being increased by one-tenth to compensate for the dilution of the 100 cc. of the water taken to 110 cc.

It is obvious that such a flask, as I have described, cannot be used in cases in which the Cl exceeds eight parts per 100,000, unless the sulphate of silver solution be of greater strength than that which I have recommended. Similar methods will, however, readily suggest themselves.

In a preliminary paper* published on this process, I mentioned that probably diphenylamine, and other compounds giving similar color reactions in the presence of concentrated sulphuric acid, might be used instead of carbazol for the *quantitative* estimation of nitrates in water. Shortly after this paper appeared, L. Spiegel† called attention to a process worked up by him, in which diphenylamine was actually used for this purpose. This is briefly described in

* *Ber.*, **21**, 3,302; this JOURNAL, **127**, 61.

† *Ber.*, **21**, 3,568.

the *Zeitschrift für Hygiene*, 1887, **2**, 189, and was quite unknown to me. Although differing in detail from that which I have devised, the principle is the same, diphenylamine taking the place of carbazol. Although Spiegel does not mention any experiments made to ascertain the influence of chlorides, it is probable that this will be found as considerable as I have found it in the case of carbazol.

The ELECTROLYTIC METHOD APPLIED to MERCURY.—SEPARATION from COPPER.

By Edgar F. Smith and Lee K. Frankel.

[*Read at the Stated Meeting of the Chemical Section, April 16, 1889.*]

The electrolytic precipitation of mercury has been successfully performed by different chemists; thus, J. B. Hannay (*Berichte d. d. chem. Gesellschaft*, **6**, 270) recommends a solution of mercury sulphate for this purpose, but gives no quantitative results. F. W. Clarke (*Am. Journal of Science*, **16**, 200; *Zeitschrift für analyt. Chemie*, **18**, 103) separated mercury from the solution of its chloride, freely acidulated with sulphuric acid, by using a current obtained from six Bunsen chromic acid cells. Classen and Ludwig (*Berichte d. d. chem. Gesellschaft*, **19**, 323) employed a mercury solution, rendered slightly acid with nitric acid, and a current affording ·5 – 1·0 cc. OH gas per minute. The time occupied in the deposition, at ordinary temperatures, was twelve to sixteen hours. Hoskinson (*Am. Chem. Journal*, **8**, 209) obtained good results with the nitrate. Smith and Knerr (*Am. Chem. Journal*, **8**, 209) employed a nitrate solution, in which there was considerable acid in excess, and with a current yielding 4 cc. OH gas per minute deposited ·1 gramme of mercury in forty-five minutes. In all of these methods, which permit of the separation of mercury from many other metals, the mercury is thrown out as a mirror-like deposit, and drops of metal are plainly discernible.

We have observed that this metal can be separated without difficulty from solutions containing a large excess of alkaline cyanide, and with a comparatively weak current. The solution used was the chloride. The conditions, time, strength of current and results are as follows, with mercury alone:

Solution Contained Hg.	Found Hg.	Per cent. Difference.	Quantity of KCN.	Total Dilution.	Time in Hours.	Current in cc. OH Gas per Minute.
Grammes.			*Grammes.*	*cc.*		*cc.*
·1945	·1953	+ ·41	·26	175	16	·2
. . .	·1948	+ ·14	·26	. . .	16	·2
. . .	·1946	+ ·05	1·30	. . .	24	. . .
. . .	·1930	— ·77	1·30	. . .	24	. . .
. . .	·1945	. . .	1·30	. . .	12	·2
. . .	·1945	. . .	1·30	. . .	12	. . .
. . .	·1945	. . .	2·60	. . .	12	·2
. . .	·1944	— ·05	·65	. . .	12	. . .
. . .	·1942	— ·14	·65	. . .	12	·2
. . .	·1956	+ ·56	·65	. . .	12	·2
. . .	·1957	+ ·61	1·30	. . .	12	. . .
. . .	·1948	+ ·14	1·30	. . .	12	·2

The deposits in these determinations were compact, rather gray in color, and showed in few cases the drop-like nature so characteristic of mercury.

For washing purposes it was found best to use water only, because when this was followed with alcohol, we noticed that the latter detached thin films of metal, causing loss in consequence. The heat of the hand is sufficient to dry the deposit, though a warm iron plate may be used. Some of the deposits were allowed to dry slowly over sulphuric acid. In our experience, with about a hundred mercury depositions, we observed but five in which there was a slight oxidation of the metal. This only occurred when a film of water remained in contact for some time with the deposited mercury.

In working with copper solutions, under conditions similar to those mentioned above, we discovered that this metal would not separate until the alkaline cyanide was completely decomposed. We, therefore, undertook a series of experiments with solutions containing both mercury and copper, hoping to effect their electrolytic separation. This seemed advisable, as the attempts in this direction had thus

far not been as successful as might be desired (See Luckow, *Zeitschrift für analyt. Chemie*, **8**, 24, and Classen, *Berichte d. d. chem. Gesellschaft*, **17**, 2,467; also *Zeitschrift für analyt. Chemie*, **24**, 247).

Our mercury solution contained the same quantity of metal as in the first experiments. Seventy per cent. of copper was added in each case. The quantity of cyanide varied from ·65 grammes to 3·9 grammes; total dilution was 200 cc., and the current strength varied from ·1 to ·4 cc. OH gas per minute. Time, six to eighteen hours. Ten experiments were performed, and notwithstanding the mercury was completely deposited, slight quantities of copper were likewise thrown out of solution.

Thirty additional experiments were made; in each the quantity of mercury was ·1945 grammes, while the copper varied from fourteen to seventy per cent. The quantity of alkaline cyanide varied from 3·9 to 8·5 grammes; total dilution remained 200 cc. The current averaged ·4 cc. to ·12 cc. OH gas per minute. Time, eighteen hours. The best results were these:

Hg Taken.	Hg Found.	Difference in Per Cent
Grammes.		*Per Cent.*
·1945	·1932	— ·66
·1920	— 1·28	
·1927	— ·92	
·1936	— ·46	
·1930	— ·77	
·1936	— ·46	
·1954	+ ·46	
·1938	— ·36	
·1923	— 1·13	
·1921	— 1·23	

These, as well as the results obtained in twenty experiments made later, seem to indicate that the presence of the copper exercises considerable influence upon the precipitation of the mercury—retards it. This fact, we think, was confirmed by ten more experiments, in all of which a slight quantity of the mercury was retained in solution, notwithstanding the current was increased to 1·2 cc. OH gas per minute, and the amount of cyanide considerably reduced.

The time of each precipitation was continued through seventeen hours.

Our attention was next directed to ascertaining whether or not a stronger current might be used to throw out the mercury, and at the same time leave the copper in solution. The results with mercury alone were

Hg Present.	Hg Found.	Difference in Per Cent.	KCN in Grammes.	Total Dilution.	Current in cc. OH Gas per Minute.	Time in Hours.
			Grammes.	*cc.*	*cc.*	
·1833	·1827	— ·27	1·5	200	2·8	16
	·1832	— ·05	1·5	200	2·8	16
	·1834	+ ·05	1·5	200	2·8	16

Using the same quantity of mercury and varying amounts of copper the results were as follows:

Hg Present.	Per Cent. of Cu Present.	Hg Found.	Difference in Per Cent.	KCN in Grammes.	Total Dilution.	Current in cc. OH Gas.	Time in Hours.
	Per Cent.		*Per Cent.*	*Grammes.*	*cc.*		*Hours.*
·1833	1	·1821	— ·65	1·5	200	3·2 cc. to 4 cc. OH per minute.	16
. . .	10	·1828	— ·27	. . .	. . .		. . .
. . .	1	·1821	— ·65	. . .	. . .		. . .
. . .	14	·1833	. . .	. . .	. . .		. . .
. . .	10	·1821	— ·65	. . .	. . .		. . .
. . .	5	·1819	— ·76	. . .	. . .		. . .
. . .	3	·1815	— ·98	. . .	. . .		. . .
. . .	5	·1834	+ ·05	. . .	. . .		. . .
. . .	3	·1836	+ ·16	. . .	. . .		. . .

which are recorded in the order obtained, and while the differences in percentage from that required vary from +·05 per cent. to —·98 per cent., and in six cases out of nine show a deficiency in the mercury, yet a careful qualitative examination of each filtrate failed to detect this metal; the error must therefore be ascribed to other causes. It may not be improper to add that these determinations and separations were not always conducted in the same platinum vessels, and, further, those used by us ranged in weight from sixty-one to 135 grammes.

Where the quantity of copper exceeded twenty per cent. of the mercury, the results were unsatisfactory.

It is well known that silver can be separated quantitatively from its cyanide solution, but whether its separation from copper could be effected in the same manner as that by which mercury and copper were separated, was undetermined; to ascertain this, we made forty experiments; ten of which resulted as follows:

Ag Present.	Copper.	Ag Found.	Difference in Per Cent.	KCN in Grammes.	Current in OH Gas.	Time in Hours.	Dilution.	
	Per Cent.		*Per Cent.*	*Grammes*	*cc.*			
	10	·1257	+ 2·78		1		200	Copper precipitated with silver.
	10	·1299	+ 6·20		1		200	
	10	·1225	+ ·16		1		200	
·1223	10	·1263	+ 3·20	·5 to 1·0	1	5 to 20	200	
	10	·1257	+ 2·78		1		200	
	10	·1244	+ 1·71		1		200	
	10	·1251	+ 2·20		1		200	
	10	·1242	+ 1·55		1		200	

Later, we diminished the quantity of copper with no better result. On increasing the quantity of cyanide, and also the strength of the current, the silver was very notably retarded in its deposition. After carefully repeating the work with no better outcome, we feel justified in saying that the cyanide method cannot be applied in the electrolytic separation of these two metals.

The current employed by us was obtained from storage batteries of the Julien form. Each cell contains nineteen plates, each of which is five and three-quarter inches square. In a long experience, with almost every form of battery, in electrolytic work, we have not had the same even, steady current for a series of hours as with the Julien form, and recommend it to all engaged in similar experiments. See further *Berichte d. d. chem. Gesellschaft*, **21**, 2,892.

University of Pennsylvania,
Philadelphia, April 13, 1889.

On the Present Condition of the Philadelphia Water Supply. Second Monthly Report.

By Samuel C. Hooker, Ph.D.

[*Read at the Stated Meeting of the Chemical Section, May 21, 1889.*]

In presenting my second report, it is with considerable pleasure that I am able to refer to a matter of very general interest and importance in connection with the water supply of this city. The northwestern portion of the city, which for years has had to endure all the inconveniences attendant upon almost continuously muddy water, will, sometime during the present month, be placed upon an equal footing with the other and heretofore more fortunate sections of the city, and will then be supplied from the East Park reservoir, instead of directly from the Schuylkill. The inhabitants of Philadelphia generally, and more particularly those of the district referred to, may be heartily congratulated on this change, which is unquestionably one of the most important improvements recently made in connection with city affairs. It may be of interest at the present time to recall some facts connected with the supply of this district.

Owing to the considerable elevation of this portion of Philadelphia, there has been no available reservoir high enough to supply it, and consequently water was pumped directly into the mains from the Schuylkill River, a process which had to be kept up continuously, regardless of what might be the condition of the river or how much it might be charged with storm water. The consequence of this is very obvious. At all times the water is more muddy, and frequently unquestionably far less wholesome than that which is supplied to other portions of the city, whose reservoir capacity is sufficiently large to allow of a plentiful supply without the necessity of drawing from the river when in its most unfavorable condition. In order to overcome these difficul-

ties land was purchased some years ago at Cambria and Thirtieth Streets, and a proposed Cambria reservoir was long talked about, but the project of construction presented so many difficulties, and promised to require a so much greater outlay of capital, per unit of storage capacity, than had been necessary in the construction of the other reservoirs, that the plan was eventually abandoned in favor of that to be put in operation in a few days.

As the height of the East Park reservoir is not sufficiently great to enable it to feed this district by gravity, arrangements have been made to pump the water into the mains after it has properly settled.

My first report has been somewhat criticised, and a number of suggestions have been made with regard to the plan of the work I have undertaken. The desirability has been urged, not only of increasing the determinations made, but also of the samples examined. It has been suggested that districts should be sought out, in which, owing to the neighborhood of the dead end of a main or to some other cause, the water is continually inferior to the average supply. The importance of these suggestions is self-evident, and it is much to be regretted that the great amount of time and labor required for carrying them out is entirely out of all proportion to that which I am able to devote to the subject. The *first* object of this investigation is to ascertain the true general condition of the water, as a whole, and when this has been done, it will be time enough to consider local causes of deterioration. With regard to the collection of the samples, I have taken no pains to select points at which, for purely local reasons, the water is likely to be exceptionally bad; neither have I endeavored to get as far away from the dead end of a main as possible, so that the water might be at its best. The samples which I am receiving are, I have every reason to believe, thoroughly representative of the water supplied to the districts in which they are drawn, and, taken as a whole, they unquestionably represent fairly the supply of the city.

With regard to increasing the number of the constituents

determined, I do not think that much would be gained at present by so doing, but as the investigation proceeds it may be found desirable to complete the chain of evidence either for or against the water, and no measures will be left untried which promise any reasonable degree of success in eliciting useful information.

It is much to be regretted that during the past month it has been found necessary to continue pumping from the Delaware at the Kensington station. The water drawn at this point, even when mixed with a large proportion from the Schuylkill, remains very decidedly inferior to the general supply of the city. In a very short time this station is to fall into disuse and no effort should be spared to avoid the necessity of having ever again to resort to it for city supply. Proper provision should be made at once to enable the Water Department, even in the case of emergency, to meet the city's requirements without having to draw a single gallon of water from this unquestionably much polluted point of the Delaware. The best thing that could be done in the public interest would be to dismantle this station in such a way that pumping here in the future would be an absolute impossibility.

Having reference to a statement made in my last report, my attention has been called by the Health Department to the fact that analyses of the water supply have been made regularly for its information during a number of years past. These analyses are withheld from the public, however, because it is feared that improper use might be made of them by individuals, and that figures might be sifted and distorted for the purpose of furthering private ends. If there is no better reasons for withholding these analyses than those which I have mentioned, it is to be hoped that, in future, matters will be regarded in a different light by the Department and that the public will be furnished with the information which rightly belongs to it. It would seem to me far more desirable that the public should be periodically told precisely to what extent the water is good or bad, how it is affected by circumstances attending its distribution, and what probable connection there is at different

times between the condition of the water supply and that of the public health. All figures, moreover, should be furnished to enable those who care to study the matter to do so.

During the period covered by this report, April 19th to May 17th, I have examined twenty-six samples of water and, taken as a whole, I am able to report very favorably on its condition. The water was, however, in a few instances extremely muddy.

The nitrates, which, during a part of the period covered by my first report, were somewhat high, have decreased considerably in quantity; the albuminoid ammonia, representing the nitrogenous organic matter in solution, is lower than that during the previous month and does not vary to any considerable extent in any of the samples examined.

I should have mentioned in my last report, that before determining the albuminoid and free ammonia, the water is carefully filtered through a good quality of paper, so as to remove as well as possible all solid particles, the presence of which would otherwise render it impossible to arrive at any correct idea of the true quality of the water, and would further make any comparison between the water supplied to the various sections of the city worse than useless. In certain cases, a filtration of this character is not able to remove some of the very fine mud held in suspension; this tells unfavorably on the analysis and is one reason, I believe, why, during the period covered by my first report, the Germantown water appeared to less advantage than that in other portions of the city.

My analyses so far show, when considered as a whole, that the actual quality (and here I have no reference to muddiness) of the Germantown water is not inferior to that of the general supply; on the contrary, I believe that if the storage capacity of the reservoir through which it passes, were sufficiently increased to allow the mud to subside properly and to avoid the necessity of drawing water at unfavorable times, it would be distinctly superior to much Schuylkill water that is supplied to other portions of the city.

The almost constantly muddy condition of the German-

town water is, however, most truly deplorable, and the attention of the authorities cannot be too earnestly called to it. The Water Department has certainly no more important task before it than the furnishing of this district with clean water

A diagram is appended, as in my last report, and as several comments have been made in regard to the former one, I would take this opportunity of mentioning that *all* the curves are not constructed to represent parts per 100,000, because if this were attempted, either the size of the diagram would have to be enormously increased, or several diagrams would be necessary.

ANALYSES OF THE PHILADELPHIA WATER SUPPLY.

RESULTS EXPRESSED IN PARTS PER 100,000.

Kensington, Beach and Vienna.

Date. 1889.	*Chlorine.*	*Free Ammonia.*	*Albuminoid Ammonia.*	*Nitrogen of Nitrates.*
April 19th, ...	·40	·0000	·0090	·08
" 26th, ...	·36	·0045	·0115	·05
May 3d, ...	·29	·0000	·0110	. . .
" 10th, ...	·37	·0030	·0080	. . .
" 17th, ...	·26	·0010	·0050	·11
Average, ...	·33	·0017	·0089	·08

West Philadelphia.

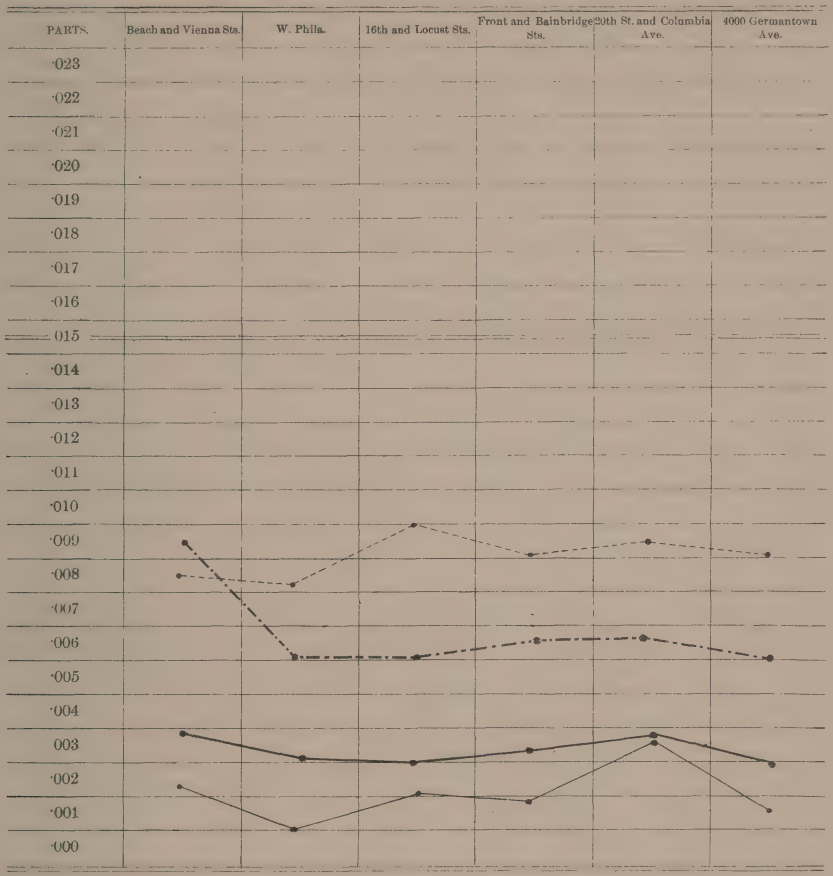
April 19th,	Not analyzed.			
" 26th, ...	·30	·0015	·0055	·077
May 3d, ...	·24	·0000	·0060	. . .
" 10th, ...	·25	·0005	·0050	. . .
" 17th, ...	·26	·0000	·0060	·077
Average, ...	·26	·0005	0056	·077

Sixteenth and Locust.

April 19th,	Not analyzed.			
" 26th, ...	·32	·0020	·0060	·088
May 3d, ...	·19	·0010	·0060	. . .
" 10th, ...	·26	·0020	·0050	·099
" 17th, ...	·26	. . .	. . .	·099
Average, ...	·25	·0016	·0056	·095

DIAGRAM SHOWING THE AVERAGE RELATIVE CONDITION OF THE WATER SUPPLY AT DIFFERENT POINTS OF THE CITY. April 19 to May 17, 1889.

(CONSTRUCTED FROM 26 ANALYSES.)



EXPLANATORY NOTES:

- - - - - - - - Nitrogen of Nitrates in parts per 10,000. Representing, when in excess, animal matter, which by natural processes of purification has been rendered harmless.

—·—·— Albuminoid Ammonia in parts per 100,000. Representing, when in excess, nitrogenous organic matter of the most dangerous type.

——————— Chlorine in parts per 1,000. Representing, when in excess, present or past sewage contamination.

——————— Free Ammonia in parts per 100,000. Representing, when in excess, decaying organic matter.

Provided that the two lower curves do not vary much in height from those given, the condition of the water may be regarded as satisfactory so long as the two upper curves remain below the double line through ·015.

It will be understood that the smaller the quantity of the substances indicated by the above curves, the more satisfactory the condition of the water. In other words, the water is most satisfactory with regard to each particular substance, at the lowest point of each curve.

Front and Bainbridge.

Date. 1889.	*Chlorine.*	*Free Ammonia.*	*Albuminoid Ammonia.*	*Nitrogen of Nitrates.*
April 19th, Not analyzed.				
" 26th, ...	·33	·0005	·0060	·077
May 3d, ...	·22	·0010	·0075	. . .
" 10th, ...	·27	·0010	·0055	. . .
" 17th, ...	·29	·0025	·0060	·088
Average, ...	.27	·0012	·0062	·082

Twentieth and Columbia Avenue.

April 19th, Not analyzed.				
" 26th, ...	·33	·0025	·0070	·066
May 3d, ...	·26	·0020	·0055	. . .
" 10th, ...	·31	·0030	·0060	·099
" 17th, ...	·30	·0020	·0060	·088
Average, ...	·30	·0027	·0061	·084

4000 Germantown Avenue.

April 19th, ...	·26	·0025	·0055	·08
" 26th, ...	·28	·0015	·0065	·088
May 3d, ...	·21	·0000	·0060	. . .
" 10th, ...	·24	·0010	·0040	. . .
" 17th, ...	·25	·0005	·0055	·088
Average, ...	·24	·0011	·0055	·082

4416 Chestnut Street.

On the Occurrence of Paraffine in Crude Petroleum.

[*An Abstract of a Thesis by E. A. Partridge, Class of '89, Univ. of Pa. Read before the Chemical Section by Prof. S. P. Sadtler.*]

It is well known that the paraffine obtained by the distillation of petroleum residues is crystalline, while that obtained directly (as in the filtration of residuum) is amorphous. Ozokerite or ceresine differs but slightly from paraffine, the principal distinction being want of crystalline structure in it as found. Other characteristics, such as the melting point, specific gravity, etc., vary in both, and so are not of importance in a comparison. Hence it has been asked, is the paraffine occurring in petroleum and ozokerite identical with that which is produced by their distillation? As crystalline paraffine could be obtained from ozokerite by distillation alone, many persons have supposed that it was engendered in the process. Recently, however, crystalline paraffine has been obtained from ozokerite by dissolving the latter in warm amyl alcohol; on cooling the greater part separates out in crystals having the lustre of mother-of-pearl. By repetition of this process, a substance is obtained that is scarcely to be distinguished from the paraffine obtained by distillation. Apparently there exists then in ozokerite, together with paraffine, other substances not capable of crystallization which keep the paraffine from crystallizing. These colloids appear to be separated by amyl alcohol in virtue of their greater solubility in that menstruum. It is also reasonable to suppose that they undergo change or decomposition by distillation.

So as petroleum residues are amorphous, and the crystalline paraffine is first produced by distillation, it has been argued that the paraffine present in crude petroleum is approximately the same thing as ozokerite.

This, however, is not sufficient to establish the pyrogenic origin of all crystallized paraffine, as crystals can be

obtained from the amorphous residues by distillation at normal or reduced pressure or in a current of steam. To explain these facts two assumptions are possible. Either the chemical and physical properties of all or some of the solid constituents are changed by the distillation, and the paraffine is changed from the amorphous into the crystalline variety, or the change produced by the distillation takes place in the medium (*i. e.*, the mother liquid) in which the paraffine exists. The change effected in ozokerite and in petroleum residues when crystalline paraffine is obtained by distillation, is to be regarded as a purification, and can be effected partially by treatment with amyl alcohol. In the same way, by repeated treatment of petroleum residuum with amyl alcohol, a substance of melting point 59° C. can be obtained, which cannot be distinguished from ordinary paraffine.

The treatment with amyl alcohol has therefore accomplished the same results as was obtained by distillation, and the action is probably the same, *i. e.*, a partial separation of colloid substance. These facts point to the conclusion that crystallizable paraffine exists ready formed in both petroleum and in ozokerite, but in both cases other colloidal substances prevent its cystallization. By distillation, these colloids appear to be destroyed or changed so as to allow the paraffine to crystallize.

It is a generally known fact that liquids always appear among the products of the distillation of paraffine, no matter in what way the distillation be conducted. This shows that some paraffine is decomposed in the operation.

The name *proto-paraffine* has been given to ozokerite, and to the paraffine of petroleum in contra-distinction to *pyro-paraffine*, the name that has been applied to the paraffine obtained by distillation from any source.

According to Reichenbach, paraffine may crystallize in three forms: needles, angular grains and leaflets having the lustre of mother-of-pearl. Hofstädter, in an article on the identity of paraffine from different sources, confirmed this statement, and added farther that at first needles, then the angular forms, and then the leaflets are formed. Fritsche

found, by means of the microscope, in the ethereal solution of ozokerite, very fine and thin crystal-leaflets concentrically grouped, and in the alcoholic solution fine irregular leaflets. Zaloziecki has recently developed these microscopic investigations to a much greater extent. According to this observer, the principal part of paraffine, as seen under the microscope, consists of shining stratified leaflets with a darker edge. The most characteristic and well-developed crystals are formed by dissolving paraffine in a mixture of ethyl and amyl alcohols and chilling. The crystals are rhombic or hexagonal tablets or leaves, and are quite regularly formed. They are unequally developed in different varieties of paraffine. The best developed are those obtained from ceresine. Their relative size and appearance give an indication as to the purity of the paraffine, and, as they are always present, they are to be counted among the characteristic tests for paraffine. Reichenbach observed that mere traces of empyreumatic oil prevented their formation.

The old method of determining the amount of paraffine in petroleum was to carry out the refining process on a small scale; that is, to distil the residue from the kerosene oils to coking, chill out the paraffine, press it thoroughly between filter-paper and weigh the residue. The sources of error in this procedure are manifold; the principal one is the solubility of paraffine in oils, which depends upon the character of both the paraffine and the oil, and also upon the temperature. The next greatest source of error is variation in the process of distillation and the difference between working on the small scale and on the large scale.

In most cases, where a paraffine determination is to be carried out, one has to deal with a mixture of paraffine with liquid oils. Now, paraffine is not a substance defined by characteristic physical properties which distinguish it from the liquid portions of petroleum. It consists of a mixture of homologous hydrocarbons, which form a solid under ordinary conditions. The hydrocarbons of this mixture show a gradation in their properties, and gradually approximate to those which are liquid at ordinary temperatures. It is a well-known fact that a separation of these homologues

is entirely impossible by distillation. It has also been ascertained that the liquid constituents of petroleum do not always possess boiling points that are lower than those of the solid constituents. This shows that we have to deal not merely with hydrocarbons of one but of several series.

When determinations of the amount of paraffine are to be made, then it becomes necessary to specify with exactness what is to be called paraffine. The most definite property that can be made use of for this purpose is the melting point. For several reasons it is convenient to include under this name hydrocarbons of melting point as low as 35°–40° C.

The method proposed by Zaloziecki for the determination of paraffine is the following: The most volatile portions of the petroleum are separated by distillation, until the thermometer shows 200° C. These portions are separated, as they exert great solvent action upon paraffine. At the same time he finds that no pyro-paraffine is formed under this temperature. A weighed portion of the residue is taken and mixed with ten parts by weight of amyl alcohol and ten parts of seventy-five per cent. ethyl alcohol: the mixture is then chilled for twelve hours to 0° C. It is then filtered cold, washed first with a mixture of amyl and ethyl alcohols, and then with ethyl alcohol alone. The paraffine is transferred to a small porcelain evaporating dish and dried at 110° C. It is then heated with concentrated sulphuric acid to 150°–160° C. for fifteen to thirty minutes with constant stirring. The acid is then neutralized and the paraffine extracted by petroleum ether. On evaporation of the solvent, the paraffine is dried at 100° C. and weighed. Zaloziecki found, according to this method, in three samples of Galician petroleums, 4·6, 5·8 and 6·5 per cent., respectively, of proto-paraffine. The method was carried out as above, with four samples of American petroleums, Colorado oil from Florence, Col.; Warren County oil from Wing Well, Warren, Pa.; Washington oil from Washington County, Pa.; Middle District oil from Butler County, Pa., all furnished by Professor Sadtler.

They were very different in physical properties and in appearance, the Colorado oil being a much heavier oil than

the others and the Washington oil being an amber oil, while the other two were of the ordinary dark green color and consistence. The losses on distillation to 200° C. were very different, being about one-tenth in the case of the Colorado oil and nearly one-half in the case of the others. The percentages of partially refined proto-paraffine in the four reduced oils (all below 200° C. off) were as follows: for the Colorado oil, 23·9 per cent.; for the Warren oil, 26·5 per cent.; for the Washington oil, 26·6 per cent.; and for the Middle District oil, 28·2 per cent.

The question now arises, what value has this determination of the proto-paraffine which may exist in an oil. As before said, a portion of the paraffine is always decomposed in distillation at temperatures sufficiently high to drive over the paraffine oils, so the yield of pyro-paraffine is always less than the proto-paraffine shown to be present originally. Zaloziecki found this in the case of the several Galician oils he examined. Corresponding to the 4·6, 5·8 and 6·5 per cent. of proto-paraffine in the several oils, he obtained 2·18, 2·65 and 2·35 per cent., respectively, of pyro-paraffine.

For the present, however, the extraction of proto-paraffine on a large scale by means of such solvents as amyl and ethyl alcohols is out of the question on account of their cost. A distillation, under reduced pressure and with superheated steam, would, however, prevent much of the decomposition of the original proto-paraffine and increase the yield of pyro-paraffine.

This study of Zaloziecki's method and the examination of American oils was suggested by Professor Sadtler and carried out in his laboratory.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, June 18, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, June 18, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Dr. S. C. Hooker, Dr. Wm. H. Wahl, Prof. S. P. Sadtler, Dr. L. B. Hall, Mr. Reuben Haines, Mr. Wm. H. Bower, Mr. Fred. E. Ives, Prof. E. F. Smith, Mr. W. L. Rowland, Dr. H. W. Jayne, Mr. Lee K. Frankel, Prof. N. Wiley Thomas, Dr. Wm. H. Greene, Prof. R. L. Chase, Mr. J. H. Eastwick, Mr. A. T. Eastwick, Mr. A. W. Allen, Dr. Geo. A. Koenig, Mr. W. W. McFarlane, Mr. W. D. Weikel, Dr. Wm. C. Day and two visitors.

The President read a letter from Mr. M. Carey Lea, transmitting specimens of the various allotropic modifications of silver obtained by him, and stating that absence from the city prevented his attendance upon the meeting.

The President presented a letter from Prof. F. W. Clarke to Dr. Greene giving information in regard to the proposed formation of a National Chemical Society. He also read a copy of a letter from Professor Remsen to Prof. A. B. Prescott, reporting unfavorably upon the suggestion to make the *American Chemical Journal* the organ of the proposed National Society.

After some discussion it was voted that Dr. L. B. Hall and Dr. Geo. A. Koenig be appointed delegates to represent the Section at the next meeting of the American Association for the Advancement of Science, upon the question of the formation of a National Chemical Society. Further consideration of the subject at present was, on motion, tabled.

Dr. Hooker read his monthly report on the Philadelphia Water Supply. The report contained facts of much importance and interest, from the sanitary standpoint, particularly with reference to the Kensington pumping station, which draws its supply from the Delaware River. The paper was referred for publication. It concluded with a resolution recommending the

condemnation of the Kensington station by the FRANKLIN INSTITUTE; the motion to adopt this resolution was carried by the Section.

Mr. Fred. E. Ives then exhibited on the screen, with the projecting microscope, specimens of various crystalline substances under the influence of polarized light.

The President then read an abstract of Mr. M. Carey Lea's paper on allotropic forms of silver and exhibited specimens of the various modifications. The subject was received with much interest by the Section.

Dr. Smith and Mr. Frankel presented a paper on "Electrolytic Separations," which was referred for publication.

Dr. Greene read a letter from E. Paternò in regard to lapachic acid and its derivatives. It was referred for publication.

Adjourned.

WM. C. DAY, *Secretary.*

ERRATUM (to minutes of April meeting): The following gentlemen were elected members of the Section at the April meeting; a statement of their election was inadvertently omitted in the minutes of that meeting: Dr. L. I. Morris, Dr. Persifor Frazer, Mr. Fred. E. Ives, Mr. Theodore D. Rand.

ON THE PREPARATION AND PROPERTIES OF METALLIC MANGANESE.

BY CHAS. BULLOCK.

[*Read at the Stated Meeting of the Chemical Section, May 21, 1889.*]

The properties of manganese, like those of iron, appear to differ according to the method used in the reduction of the metal. When obtained from the oxide by heating with carbon, most authorities agree in the statement that the metal oxidizes so readily in the air that it can be preserved only under "rock oil," or in well sealed vessels. In water it is said to "oxidize rapidly, with evolution of hydrogen, and crumbles into a dark gray powder."

Cast manganese containing eight per cent. of iron is said to be unalterable in the air.

In the year 1869, some manganese prepared by me after the process of Brunner (the reduction of the chloride mixed with fluorspar, by means of sodium) was found to have as little tendency to oxidation as iron.

Repeating recently this process, pure chloride of manganese was fused in a clay crucible and poured on a stone slab, when cold it was pulverized and mixed with an equal weight of powdered fluorspar. This mixture, divided into portions of one ounce, was introduced into a French clay crucible, previously heated to redness. Eighty grains of sodium, cut into small pieces and freed from naphtha, being added to each portion, the crucible was covered, and reaction allowed to take place before adding another charge. After six ounces of the mixture had been added, the contents of the crucible was covered with fused chloride of sodium in powder, the cover replaced and the heat carried to quiet fusion. After the flux became entirely fluid, the heat was continued for ten minutes. The crucible was then removed from the fire, and after cooling the metal was found as a button at the bottom.

Three crucibles, of the capacity of eight fluid ounces each, were used at a time in a furnace without artificial blast. Care is necessary not to urge the heat too high, otherwise the crucibles will not resist the action of the fluorspar flux. The French clay crucibles were used on account of their greater freedom from iron and silica; they also resist the flux better than the Hessian, black lead or iron crucibles.

The yield of manganese under favorable circumstances, was about twenty per cent. of the chloride used.

Reduction was also tried by using fused chloride of sodium without fluorspar, the yield of metal was much less and differing in some of its properties from that obtained with the use of fluorspar. Manganate of soda was formed when sodium chloride alone was used as a flux.

Manganese thus obtained is very brittle, with a steel white fracture, so hard that a file will scarcely touch it, the edges of the fractures scratch, and almost cut, glass.

The metal retains the brightness of a fractured surface after prolonged exposure to the air, and appears not more disposed to oxidation than iron. It is entirely passive to magnetic attraction.

The specific gravity of the metal obtained when fluorspar was used was 7·072, when re-melted under fused sodium chloride, the sp. gr. rose to 7·153.

The metal obtained without the use of fluorspar was less brittle, and had a different fracture; its sp. gr. was 7·231.

Authorities differ regarding the sp. gr. of manganese, ranging it from 6·85 to 8·013.

An examination of the metal obtained, using fluorspar as a flux, showed the absence of iron, and the presence of calcium, demonstrating the reduction of some of the latter metal from the spar. This may account in a measure for the increased sp. gr. on re-melting under sodium chloride, as also the greater sp. gr. of the metal when the spar was not used. As calcium has the sp. gr. of 1·57, a small amount alloyed with the manganese would sensibly affect its gravity.*

On ACETO-METANITROBENZOIC ANHYDRIDE.

By Wm. H. Greene.

[*Read at the Stated Meeting of the Chemical Section, May 21, 1889.*]

In the reaction of acetyl chloride with silver metanitrobenzoate, L. Liebermann† claimed to have obtained metanitrobenzoyl acetic acid, a reaction which would be inexplicable and without analogy. In the course of another investigation Bischoff and Rach‡ took the opportunity of studying the action of acetyl chloride on the silver salt of *o*-nitrobenzoic acid, and found that the reaction did not take place in the sense indicated by L. Liebermann.

Under the name acetylmetanitrobenzoic anhydride, Beilstein in his *Organische Chemie* (ii, 786) describes the product supposed by Liebermann to be metanitrobenzoyl acetic acid, but the properties mentioned accord as little with those which this anhydride should exhibit, as with those which

* Sp. gr. of iron, gray, ... 7·1
" " white, ... 7·5
" " pure, ... 7·84
—*Roscoe and Schorlemmer.*

† *Berichte*, **10**, 863.

‡ *Berichte*, **17**, 2,799.

would be expected in the acid Liebermann thought he had obtained.

A preparation of this compound, according to the indications of L., by the addition of dry silver metanitrobenzoate to an excess of cold acetyl chloride, and pouring the product into water, yielded an acid fusing between 126° and 137°. 0·1866 grammes of the silver salt of this acid yielded 0·0731 grammes silver.

Ag found, 39·17 per cent. Ag calculated for nitrobenzoate, 39·42 per cent.

The acid is metanitrobenzoic, regenerated from the silver salt employed.

By the reaction of sodium metanitrobenzoate with acetyl chloride, extraction of the product with absolute ether, and evaporation of the latter, aceto-metanitrobenzoic anhydride may be readily obtained, as also by exposing silver metanitrobenzoate to vapor of acetyl chloride and extraction with absolute ether in the same manner. It crystallizes in colorless needles, fusible at 45°, and remaining in superfusion at a much lower temperature. It is insoluble in water by which it is not at once decomposed when crystallized, so that it may be washed with dilute sodium carbonate and water, and quickly dried between filter papers without change. The presence of either alcohol or water in the ether used for extraction results in the complete decomposition of all the anhydride.

On the Present Condition of the Philadelphia Water Supply. Third Monthly Report.

By Samuel C. Hooker, Ph.D.

[*Read at the Stated Meeting of the Chemical Section, June 18, 1889.*]

In my last report presented to the Section a month ago, I recommended that the Kensington pumping station be dismantled. I did not, however, deal with the Kensington supply as fully as I now propose to do, as there appeared to be a reasonable hope that this station would only be resorted to, in the immediate future, in the event of an unexpected break-down occurring at one or other of the stations on the Schuylkill.

This hope, which was based upon statements emanating from the Department of Public Works, has, however, been shattered during the past month, and the importance of the subject is so great that I feel I cannot do better than devote this report entirely to its consideration.

I wish it, at the outset, to be distinctly understood that whatever is said in this report refers exclusively to the water drawn from the Delaware at the Kensington station, and does not have any bearing whatever upon the city supply as a whole. While I shall presently speak strongly against the water pumped at the Kensington Works, the experience of the past month has strengthened the fairly favorable conclusion to which I had previously come, regarding the actual quality, aside from muddiness, of the Schuylkill water, which, as is well known, forms the bulk of the city supply.

The Kensington district is at present supplied from the Delaware at Kensington, from the Delaware at Lardner's Point, and from the Schuylkill.

Two thirty-inch mains, the one conveying water from the Wentz Farm reservoir, the other from the Schuylkill, make connection with the Lehigh basin, which supplies the dis-

trict. The Kensington pump also discharges into the Lehigh basin.

In spite of all efforts which can be made by the Water Department, under existing circumstances, the water carried through the two mains just referred to, from the Schuylkill and from the Wentz Farm basin, is not sufficient for the requirements of the neighborhood, and consequently the level in the Lehigh basin gradually sinks, pressure diminishes, and finally complaints of short supply reach officers of the Department. Nothing remains but to start up the pump at Kensington, and to continue drawing water from the Delaware until the reservoir is again filled. I thoroughly believe that the necessity of abandoning the Kensington station is fully realized by the Chief Engineer of the Water Department, but he is powerless to cause this to be done until some adequate provision is made for meeting the requirements of the district.

The bulk of the water drawn at the Kensington Works is supplied to the sixteenth, seventeenth, eighteenth, nineteenth and thirty-first wards. This district, as is well known, is the unhealthiest portion of the city. That the water is in a great measure responsible, there can be no doubt; to say that it is entirely responsible, would unquestionably be stating the case too strongly.

It is proposed to carry a forty-eight-inch main from the Schuylkill, in place of the thirty-inch main now existing, but this cannot be done without money, and until the sum necessary for this purpose is appropriated, pumping from the Delaware at Kensington must continue to a greater or less extent.

For years past the money which has been placed at the disposal of the Department has been very far short of that required for its imperative needs, and this state of affairs promises to continue unless some action is taken by the general public in asserting its rights and insisting that they shall be respected.

Whatever difference of opinion may exist regarding the wholesomeness of the Schuylkill, there is absolutely none possible regarding that of the Delaware at Kensington, and it

cannot be too strongly insisted that this foul, sewage-polluted water shall be no longer used for city supply, even though its poisonous and filthy character is partially or entirely disguised by admixture with large volumes of water from the Schuylkill and from Lardner's Point.

It is simply impossible for the sewage discharged into the Delaware, in the neighborhood of the Kensington Works, to be in any degree purified before it is taken up by the pump and distributed to the helpless population of the sixteenth, seventeenth, eighteenth, nineteenth and thirty-first wards. What wonder, then, that the Kensington district is a very hot-bed of disease in this city!

For nearly thirty years, this water from the Delaware at Kensington has been repeatedly condemned as *unfit for use* by Health Boards, by the engineers of the Water Department, by the experts who have examined into the matter, by every one, in fact, whose scientific knowledge has been sufficient to enable a clear estimate to be formed of the danger of supplying this sewage-saturated water to the community. Common sense rebels against it, the records of the Health Office silently protest against it, and yet for thirty years this pumping from the Delaware at Kensington, from a station which ought never to have been established, has been continued.

For a great number of years it has been the purpose of the various administrations of the city to abandon the Kensington Works, and it may be well to inquire how it happens that in spite of such good intentions these works still exist. The recommendations suggested by the various engineers of the Water Department, if carried out promptly at the time they were made, unquestionably would have enabled the Kensington station to fall into disuse, but unfortunately they were allowed to remain so long unacted upon, that when finally put into effect, instead of being able to supplant the Delaware supply for which they were originally devised, they were only able to meet the additional requirements of the district, due to its growth in the meantime.

It has been argued that the quantity of water pumped at

Kensington is insignificantly small compared with the total supply of the city. So much the better; but instead of being a good reason for the water to be tolerated, it makes substitution of better water all the easier, and therefore all the more to be insisted upon.

Let me now refer to a few extracts from the reports of the Board of Health. The first is taken from the report for the year 1862, p. 13:

"One of the most serious and aggravated nuisances which "has attracted the attention of the Board was the water "supplied by the Kensington Works. After a careful "investigation, based upon personal observation, as well as "the experience of several physicians practising, and the "analysis of a practical chemist, the Board, in May last, "declared the water therefrom furnished to be a nuisance, "prejudicial to public health, and so notified Councils. "* * * *We are of the opinion that the only permanent remedy "will be the total abandonment of the Kensington Works."*

In the report of the Board of Health for 1866, p. 10, occurs the following:

"*All things considered the water is a sanitary evil of so "dangerous a nature to the health of the inhabitants of those wards "through which it is distributed, as to demand at the hands of "Councils its immediate disuse.*" (The Chief Engineer, after an allusion to the alterations since made, says: "*I regard it as "certain that the supplying of pure, or in any considerable degree "suitable, water, for domestic purposes, from the river Delaware at "the location of the Kensington Water Works, is impossible.*")

"Notwithstanding the improvement in the induction pas- "sage from the river to the pumps there has been no "improvement in the water itself, nor can there ever be whilst "the present supply of Kensington water is derived from the "river Delaware at the present location. It will be evident "to every disinterested visitor to the Kensington Water "Works that a supply of pure water is impossible. The "sewers opening into the river Delaware discharge their con- "tents at a rate of an average of about 13,000,000 gallons "daily, which necessarily includes every description of

* The italics in this and in the following quotations are my own.

"impure and refuse matter from the city, and of late years "this impurity is much increased by the construction and "connection of numerous water-closets with the sewers, from "both public and private dwellings. A further deterioration "necessarily occurs from the emptying of Gunner's Run and "Cohocksink Creek into the Delaware, together with the large "amount of human and other offal deposited in the river at "Richmond. * * *

"The action of the tides, the movements of steamboats "and the general traffic on the river, keep in suspense and "carry a large portion of the impurities from the sewers "from Gunner's Run and the Cohocksink Creek far beyond "the present mouth of the induction tube at the end of the "wharf. * * * When we know from our bills of weekly "mortality that out of 277 deaths from *cholera Asiatica*, 132 "(or 47 per cent.) have occurred in those wards supplied with "the Kensington Delaware water, we think we shall be borne "out in the opinion that the prevalence of the disease in "those districts is not only occasioned by the use of the "water as a prominent cause, but that the water has so "deteriorated in quality as to make it unfit for domestic "purposes, dangerous to health and life, and therefore your "committee would declare it to be a nuisance prejudicial to "health, and would offer the following:

"*Resolved*, That the Kensington water supply as taken "from the Delaware is a nuisance prejudicial to public health, "and that Councils be urged by this Board to discontinue the "supply at the earliest practicable moment, as the only "remedy for the removal of the nuisance and the protection "of the health of the district supplied therewith."

If this was the condition of affairs nearly twenty-five years ago, with how much more force do these arguments apply at the present time, when the amount of the sewage flowing into the river Delaware in the neighborhood of the Kensington pumping station has been ever on the increase.

The following extract is taken from the report for 1871, p. 28:

"The immense quantity of filth of every description "deposited in the river from the common sewers, estimated

"at *over 13,000,000 gallons daily*, and decomposing organic "matter always floating about the wharves, which is carried "up and down the river front by the tidal currents, and con- "stantly agitated by the general traffic upon the river, must "of necessity have a deleterious effect upon the water, even "at a distance from the shore. * * * *In the opinion of this "Board, water taken from the Delaware River at any point "along the city front is totally unfit for domestic use.*"

Again, in the report of the Board of Health to the Mayor, for 1882, p. 13:

"The water pumped at the Kensington Works is unfit "for domestic use, and this station should be abandoned."

* * * "This recommendation has frequently been "made before, but it has never been heeded. It would "appear reasonable to infer that the high death rate in the "wards supplied with this water has some connection with "the fact above stated."

The following occurs in the report of the Chief Engineer, Philadelphia Water Department, for 1883, p. 45:

"The Delaware, along the city front, is the recipient "sooner or later, of the sewage refuse and street washings of "a city area occupied by a population probably exceeding "800,000. These waste matters are borne up and down by "the tides and usually pass and repass the city several times "before taking their final departure. Under these circum- "stances, whatever may be the volume of the stream, it is by "necessity polluted and is not suitable for immediate and "habitual daily use. *In especial is the vicinity of the Kensing- "ton station marked by an accumulation of the foulest materials.* "Its central position insures its getting the full benefit of "the city's sewage, and in addition the Aramingo Canal—an "open sewer of large dimensions and choked with filth—dis- "charges in its immediate vicinity. The water taken thence "is utterly unfit for human consumption."

These extracts might be indefinitely multiplied, chemical analyses might be quoted, health statistics dwelt upon —but to what purpose? The evidence I have already presented seems to me so overwhelming that it would gain nothing in force by such additional arguments.

If the arguments against the Kensington station carried only one-tenth of the weight of those actually existing, there would still be sufficient reason to require its immediate removal.

The existence of the Kensington station through the past thirty years has been a sufficient disgrace to the city. Let it be tolerated no longer. Let public opinion express itself strongly, unmistakably. Let the newspapers of this city unceasingly agitate the matter. Let the learned and other societies engage in the contest. Let individual influence be exercised. The Kensington pumping station will then exist only as a memory of the past, to be long remembered for the desolation it has wrought in many families, but not to be feared for that which it also threatens, as at the present time, in the future.

Let us not be satisfied with any half measures, for so long as the Kensington pump remains it will be liable to be put into operation at any time. The station must be completely dismantled and pumping rendered absolutely impossible in the future.

Finally, let me ask you gentlemen, who represent the most prominent of the chemists of this city, and who by your attainments and knowledge are especially qualified to give judgment on this most important subject, unanimously to recommend to the INSTITUTE the passage of the following resolution:

"That the FRANKLIN INSTITUTE most strongly condemns the use of the Delaware water at Kensington for city supply and that it urges Councils to take immediate steps to render possible the abandonment of the Kensington pumping station."

By passing this resolution without a dissenting vote, I feel that you will confer a great benefit on the city and add to the good work for which the FRANKLIN INSTITUTE has been noted in the past.

ABSTRACTS.

ALLOTROPIC FORMS OF SILVER. BY M. CAREY LEA.—In the *American Journal of Science* for June, 1889, Mr. M. Carey Lea has a paper on "Allotropic Forms of Silver." His experiments show that metallic silver may exist in a perfectly soluble form, dissolving easily and abundantly in water. Starting from this, it may show all degrees of solubility down to absolute insolubility, still, however, existing in an allotropic form and quite distinct from normal or ordinary silver. The solutions formed are as perfect as those of any other soluble substance.

There are three modifications of this allotropic form:

A. The Soluble Form.—A solution of ferrous citrate (or of a mixture of ferrous sulphate and sodic citrate) is added to a solution of silver nitrate, the mixture well stirred and allowed to stand for ten or fifteen minutes. The lilac-blue precipitate is then washed on a filter with a five per cent. or ten per cent. solution of nitrate, citrate or sulphate of ammonia or of soda, in any of which salts it is perfectly insoluble. The color changes on washing to a deep blue. To remove the iron as far as possible, repeated solution in water and re-precipitation by ammonic nitrate is necessary, the ammonia salt being finally displaced by washing with ninety-five per cent. alcohol. The aqueous solution of this allotropic form of silver is blood-red. Optical examination proved it to be a true solution, and not a mere suspension of a finely-divided precipitate. "The inference, therefore, seems to be very strong that there exists an allotropic form of silver, freely soluble in water. This is a property so exceptional in a metal that I have admitted it with much hesitation. The principal arguments are as follows:

"The contents of silver in the various products was very carefully, and, I believe I may say, quite accurately determined; it was extremely high, always above ninety-seven per cent. As already remarked, this virtually excludes the presence of all other elements, except hydrogen and possibly oxygen. These elements were carefully searched for, but their presence could not be detected. To suppose that we had to do with a mixture in which some compound of silver was mixed with metallic silver was not possible, for, as the whole was soluble, we should still have to admit the solubility of silver.

"We have, consequently, to deal with a substance containing over ninety-seven per cent. of silver, and neither hydrogen nor oxygen in combination with it—the remaining two or three per cent. fully accounted for by ferric oxide and citric acid, determined as present as accidental impurity; the substance itself readily amalgamating with mercury by simple friction, nevertheless abundantly soluble in water. If I had been able to find any other explanation for these facts, without admitting the solubility of silver, I should have adopted it. But none presented itself.

"Whether, in solution, it exists as a hydrate—that is, in more intimate combination with one or more equivalents of water—cannot be said with entire certainty; but the easy amalgamation with mercury seems hardly to favor that view."

B. The Insoluble Form.—The first and soluble modification of the allotropic form of silver was produced, as shown above, by precipitating by an alkaline nitrate, citrate or sulphate. The second and insoluble form is produced by precipitating by magnesium, cupric, ferrous or nickel sulphate, or by potassium bichromate or ferrocyanide, or by barium nitrate, or even by silver nitrate. If any one of these salts is employed in extremely dilute solutions as the precipitant, the resulting precipitate is insoluble in water. If it is treated with a concentrated solution of any of the above salts, it becomes, strange to say, once more soluble in water.

This insoluble form is best seen when applied as a thin film to paper by a brush, enough water being added to give it a paste-like consistency. This film is of a greenish color, blue in certain lights, yellow in others ; the yellow being the more pronounced in proportion as the washing is thorough. On drying, the lustre is remarkable, a perfect mirror being obtained. This insoluble form, after drying at 100°C., contained 97·96 per cent. silver. "The remaining 2·04 per cent. consisted of ferric oxide and citric acid."

C. The gold-yellow and copper-colored silver is produced by the reduction of silver tartrate by ferrous tartrate. The resulting precipitate is first glittering red, then changes to black, and on the filter has a beautiful bronze appearance. The silver nitrate is entirely converted into this allotropic form, which is insoluble in water, and dries to lumps exactly resembling highly-polished gold. A paste of it extended over glazed paper, dries with the splendid lustre of gold leaf. The percentage of silver present = 98·75. Occasionally, a spontaneous reversion to normal silver occurs, the latter being extremely beautiful and resembling the finest frosted jeweler's silver.

All of the above allotropic forms have the following properties in common :

(1) *That of drying with their particles in optical contact* and consequently forming films and mirrors as above described.

(2) *The halogen reaction.* When any of the films on paper are dipped in a solution of sodium hypochlorite of ferric chloride, or of iodine dissolved in potassium iodide, magnificent intense shades with metallic reflections are produced. They often remind one of the color of a peacock's tail and are caused by interference. This characteristic forms one of the principal reactions for distinguishing allotropic silver from ordinary silver.

(3) The stronger acids, even when much diluted, instantly convert the allotropic form of silver into normal gray silver, without the slightest evolution of gas.

(4) All of these allotropic forms are easily reduced to an impalpable powder. In addition to these four points, Mr. Lea states that all of his products readily form an amalgam with mercury.

Mr. Lea has been at work upon this subject for over three years. He expects to have a second paper in the July number of the *American Journal of Science*. The properties of these allotropic forms of silver discovered by him are certainly extraordinary. Indeed, any *one* of the properties of these products is remarkable. It is remarkable that silver can be obtained in a form having all the color and brilliancy of gold. It is remarkable that while having thus the lustre of a metal and also the metallic property of amalga-

mating with mercury, it still is friable and easily reduced to powder. But most remarkable of all is the fact that it is freely and abundantly soluble in water. Certainly this property is unique. In the entire list of metals there is none that possesses anything like it.

Mr. Lea's investigations have opened a most interesting field of research, that will probably produce results of the highest importance. P.

On Lapachic Acid and its Derivatives.

By E. Paterno.

[*Communicated by Dr. W. H. Greene, at the stated meeting of the Chemical Section, held June 18, 1889.*]

In the last number of the *American Chemical Journal* (**11**, No. 4, April, 1889, p. 267) which reached me yesterday, I have read an important note by W. H. Greene and S. C. Hooker, in which is proved the identity of the coloring matter of Bethabarra wood with lapachic acid. In ending their note the authors propose to study lapachone and suggest that certain reactions observed by them lead to the belief that this compound has not the constitution provisionally assigned by me in 1882.*

I must draw the attention of these two chemists to the fact that in my memoir, after having stated that the constitution of lapachone was perhaps the most difficult and important point to determine, I terminated by saying, that all my considerations had a very limited value and I dwelt on it but a moment, with the sole design of showing the importance and the range of the argument of which I had undertaken the study.

It is indeed true that since 1882 I have published nothing on lapachic acid. I have been occupied with other matters, it has been difficult for me to obtain first materials, and I did not desire to publish the results in parts, especially when I had reserved the right of continuing the research. However, that I have never abandoned the work is shown by the fact that in my research on Raoult's law, published conjointly with Nasini in 1886,† we proved that lapachone is not a polymeride of lapachone as I at first supposed, but that it corresponds to the simple formula $C^{15}H^{14}O^3$, and I said that while the polymeric quinones so far studied are brown substances, only slightly soluble and having fusing points much higher than the corresponding quinones, these great differences in external characters are not observed between lapachic acid and lapachone. Since that time, as I have besides announced a few months ago,‡ I have continued

* *Gazzetta Chimica*, **12**, 337. † *Ibid*, **16**, 262. ‡ *Ibid*, **19**, 3.

this research with greater industry, and by applying Raoult's method I have shown that the acetyl derivative of lapachic acid fusing at 131–132°, for which I had advanced a complex formula, corresponds rather to that of a diacetic derivative of lapachic acid or of lapachone or more probably another isomeride of this substance; and in a series of researches, that I may say are complete and which were in part made together with Sig. Minimi, I have entirely reconsidered the study of those derivatives of lapachic acid of whose constitution I entertained doubts, and in particular lapachone, the diacetyl derivative and the magnificent substance crystallizing in splendid bronze-red laminæ. Of lapachic acid and lapachone we have studied the oxime and hydrazin compounds, we have obtained the quinone corresponding to the diacetyl derivative, we have prepared and studied the triacetyl derivative, corresponding to the reduction derivative of lapachic acid, the compound of lapachic acid with thiophen has been prepared, and in this manner we have collected together a considerable number of facts which completely elucidate the constitution of lapachone and many other derivatives of lapachic acid.

I am sure that Messrs. Greene and Hooker will, after what I have exposed, allow us time to publish our labors and desist from the further investigation of lapachic acid derivatives, at least until after the publication of our researches.

ELECTROLYTIC SEPARATIONS.

By Edgar F. Smith and Lee K. Frankel.

[*Read at the Meeting of the Chemical Section, June 18, 1889.*]

I. SEPARATION OF CADMIUM FROM COPPER.

The results obtained in the electrolysis of cyanide solutions of mercury and copper, as well as the knowledge gained from our experiments in separating cadmium from zinc, induced us to try whether it would be possible to effect the evaporation of cadmium from copper in cyanide solution. The only electrolytic method pro-

posed for the separation of these metals is that recommended by Smith (*Am. Chem. Journal*, **2**, 42), in which solutions containing a definite amount of free nitric acid were employed. We experienced no difficulty in making a complete separation, after ascertaining the proper current strength. The conditions most favorable to the separation were essentially the same as those recorded in our former papers, viz: a dilution of 200 cc.; 5·5 grammes of potassium cyanide in each experiment, and a current generating ·28 cc. oxy-hydrogen gas per minute. Time sixteen to twenty hours. The results obtained were as follows:

Cadmium present.	*Cu present.*	*Cadmium found.*
	I.	
·2426 grs.	50 per cent.	·2420
	II.	
·2318	50 per cent.	·2331
	"	·2309
	"	·2315
	III.	
·1024	100 per cent.	·1028
	"	·1019
	"	·1020
	"	·1032
	"	·1033
	"	·1034
	"	·1014
	IV.	
·2046	100 per cent.	·2034

Copper was not found in any of the deposited cadmium, nor did we discover any of the latter metal in the filtrate containing the copper. The cadmium deposit invariably showed the gray color characteristic of it.

II. ACTION OF THE CURRENT UPON METALLIC SULPHOCYANIDES.

It is well known that in the electrolysis of the sulphate or nitrate of manganese the oxide of this metal separates upon the positive pole. We have found that if an excess of potassium sulphocyanide be present no such deposition occurs, but, on the contrary, the metal itself will separate as

a grayish white, compact deposit upon the negative pole or the vessel attached to it. The addition of a sulphocyanide to the manganese solution undergoing electrolysis, after the oxide has already separated, will cause the solution of the latter. The current necessary for the deposition of metallic manganese, under the conditions mentioned above, should be feeble. The metallic deposit is inclined to rapidly oxidize, and whether manganese can be successfully determined in a quanitative way after this manner will depend very much upon whether we can prevent its oxidation during the drying process.

Nickel, cobalt, iron and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current.

CHEMICAL LABORATORY, UNIV. OF PA.,
PHILADELPHIA, June 18, 1889.

ON THE CONSTITUTION OF LAPACHIC ACID AND ITS DERIVATIVES.

BY SAMUEL C. HOOKER AND WM. H. GREENE.

[*Read at the Meeting of the Chemical Section, held Tuesday, May 21, 1889.*]

In 1857, Arnoudon* described, under the name taiguic acid, a yellow coloring matter existing in the Taigu wood of Paraguay; nine years later, Stein † described as greenhartin a similar matter which he had extracted from the greenheart of Surinam. In 1879, Paterno ‡ proved the identity of these substances with the lapachic acid obtained by Siewert from the Lapacho tree of South America. Finally, we have recently found the same substance in a South African wood, the Bethabarra.§

Paterno,‖ in an admirable research published in the

* *Comptes rendus*, **41**, *1,152*.

† *Jour. für prak. Chemie*, **99**.

‡ *Gaz. Chim. Ital.*, **9**, 506.

§ *American Chem. Journal*, **11**, 267.

‖ *Gaz. Chim. Ital.*, **12**, 337–392.

Gazzetta, 1882, has assigned to lapachic acid, with a very great degree of probability, the following constitutional formula:

$$C_{10}H_4 \begin{cases} O_2 \\ CH = CH - C_3H_7 \\ OH \end{cases}$$

Oxy-amylene-naphthaquinone.

The results from which this formula are mainly deduced are the following:

Lapachic acid gives a series of stable salts, but all experiments failed to reveal the true acid group, COOH.

On distillation with zinc dust, naphthalene and isobutylene were obtained.

On oxidation with nitric acid, phthalic acid was formed.

By reducing agents, a hydrolapachic acid was obtained, which rapidly absorbed oxygen, becoming reconverted into lapachic acid.

A monacetyl derivative was obtained.

Hydriodic acid and phosphorus gave a liquid hydrocarbon, which was taken to be amyl-naphthalene.

In the course of the study of this acid, Paterno prepared several compounds, which he was only able to explain satisfactorily by the assumption that two molecules of the acid had taken part in the formation of each of their molecules.

By the action of concentrated sulphuric acid on lapachic acid, a compound crystallizing in beautiful red needles is formed, which has precisely the same percentage composition as lapachic acid. This compound, which is known as lapachone, was assigned the following formula, by Paterno:

$$OH.C_{10}H_4(C_5H_9)\begin{matrix} O.O \\ O.O \end{matrix}C_{10}H_4(C_5H_9).OH.$$

Lapachone is insoluble in alkaline carbonates; it is soluble in caustic alkalies only after boiling for some time. According to Paterno it separates from the alkaline solution on cooling and is almost completely precipitated unchanged on the addition of acids.

While recently engaged on the study of the coloring matter of Bethabarra wood, subsequently proved by us to be lapachic acid, we obtained an orange-red quinone-like substance. In the course of our experiments with this compound we observed a number of reactions which, when we had afterwards identified the compound as lapachone, did not agree with Paterno's view of its constitution.

We found that lapachone shows many of the characteristics of a chinone. It gives a white crystalline compound with acid sodic sulphite, which is reconverted by acids and alkalies into the original substance. It forms compounds with hydroxylamine and ammonia with great readiness, and gives the quinone color reaction of Bamberger.

These reactions are obviously not reconcilable with the formula given above and point to the probability that lapachone is $C_{15}H_{14}O_3$ and not $C_{30}H_{28}O_6$.

A determination of the molecular weight of lapachone, by Raoult's method, gave figures confirming this supposition, thus proving that only one molecule of lapachic acid is concerned in its formation, a result borne out by other facts.

Calculated for Paterno's formula $C_{30}H_{28}O_6$	*Calculated for* $C_{15}H_{14}O_3$	*Found.*
484	242	255

It remains, therefore, to explain how a substance having such strong acid tendencies as lapachic acid, dissolving with ease in alkaline carbonates, can be converted into an indifferent compound like lapachone, and yet retain the same percentage composition.

Although Paterno's formula of lapachic acid cannot be considered in any way proved, it lends itself well to the explanation of the formation of lapachone, and in this way considerable indirect proof is furnished of the probable correctness of Paterno's views in regard to lapachic acid.

It seems lawful to assume, that under the influence of strong mineral acids (concentrated nitric acid in the cold acts similarly to concentrated sulphuric acid as shown by Paterno) lapachic acid takes up a molecule of water

giving rise to an intermediate compound, which is at once decomposed by the acid, again splitting off water, but in a different direction. This is shown in the following equation:

$$C_{10}H_4\begin{cases}O_2\\CH\\OH\end{cases} = CH.C_3H_7 + H_2O$$

Lapachic acid.

$$= C_{10}H_4\begin{cases}O_2\\CH_2\\OH\end{cases} - CH(OH).C_3H_7$$

Oxy-hydro-lapachic acid.

$$= C_{10}H_4\begin{cases}O_2\\CH_2\\O\end{cases}\!\!\diagdown\!\!\diagup CH.C_3H_7 + H_2O$$

Lapachone.

The fact that phthalic acid is produced by the oxidation of lapachic acid, would appear to furnish proof that all the side groups are situated in the same benzene nucleus, and consequently whether lapachic acid be a derivative of α- or β-napthaquinone the (OH) group must be in the ortho position to the amylene chain: this favors the probability of the occurrence of the above condensation.*

This view of the constitution of lapachone, *i.e.*, regarding it as a derivative of naphthofurfuran, agrees very thoroughly with all its properties and reactions so far observed. It has, moreover, received direct confirmation from the result of an experiment, which was made to obtain, if possible, corroboration of our views.

Paterno states, as already mentioned, that lapachone is insoluble in caustic alkalies in the cold, but dissolves on heating, and is, in part, deposited from the filtered solution unchanged as it cools.

This observation, seemed at variance with our idea of the constitution of lapachone, and we consequently carefully repeated Paterno's experiment. The insolubility of lapachone in alkaline carbonates and caustic alkalies in

* It is, of course, possible, though scarcely probable, that lapachic acid is derived from β β-naphthaquinone, in which case the relative positions of the amylene chain and the hydroxyl group would be the para.

the cold is readily explained by the constitution we have assigned to it, and its solubility on boiling is best accounted for by the supposition that the furfuran ring is split by the action of potash, that one molecule of water is taken up with the formation of a salt of the compound:

$$C_{10}H_4 \begin{cases} O_2 \\ CH_2,CH(OH).C_3H_7 \\ OH \end{cases}$$

Oxy-hydro-lapachic acid,

which we had previously supposed to exist as an intermediate product in the formation of lapachone. This explanation proved quite satisfactory, for on neutralizing with acetic acid, a red oil was obtained which, in the course of an hour or so, solidified to a yellow crystalline mass.

Analysis proved it to have the expected composition. The tendency of the new substance to pass into lapachone under the influence of dilute mineral acids is very great, and hence if dilute HCl acid be used for the precipitation, either a mixture of lapachone and the new compound, or lapachone only is obtained.

We have not yet succeeded in preparing the potassium salt of the new substance in a crystalline form, but as its barium salt, which crystallizes very readily in bright orange needles, closely resembles lapachone, it is not improbable that the potassium salt may have a similar appearance, which would account for Paterno's supposition that the crystals deposited on cooling and before the addition of hydrochloric acid were crystals of lapachone. It is right to add that the fusing point of these crystals was found by Paterno to be almost identical with that of lapachone.

The salts of the new compound as might be expected dissolve to the same intense red color as those of lapachic acid. It melts at 125°, and is very readily soluble in most ordinary solvents. It may be obtained in comparatively large crystals, by spontaneous evaporation of its solution in alcohol or acetic acid.

By the action of bromine on lapachic acid in acetic acid solution, Paterno obtained a compound which he regarded

as monobrom-lapachic acid and to which he assigned the formula

$$C_{10}H_4\begin{cases} O_2 \\ CH{=}CH.C_3H_7 \\ OBr \end{cases}$$

Considering the properties of this compound and the probable constitution of lapachic acid, its formation would seem to be better explained by the supposition that an addition product is first formed, and that this by splitting off hydrobromic acid, gives rise to the formation not of brom-lapachic acid but of brom-lapachone, thus :—

$$C_{10}H_4\begin{cases} O_2 \\ CH{=}CH.C_3H_7 \\ OH \end{cases} + Br_2$$

$$= C_{10}H_4\begin{cases} O_2 \\ CHBr - CHBr(C_3H_7) \\ OH \end{cases}$$

$$= C_{10}H_4\begin{cases} O_2 \\ CHBr \diagdown \\ O \quad \diagup CH.C_3H_7 \end{cases}$$

We are at present endeavoring to prove the truth of this supposition and have already observed some important facts tending to show the correctness of our views.

The formation of several of the other compounds obtained by Paterno, would appear to be better explained in a similar manner to the foregoing than by the formulæ he has assigned to them. We prefer, however, to leave the discussion of these until our work has progressed further. In the meantime, we wish to say that, although we are hopeful further experiments will justify our present conclusions, we do not regard them as of necessity final and have only been induced to make this preliminary communication to ensure to ourselves the undisturbed continuation of the work, which, owing to many causes, can not, unfortunately, proceed with as great rapidity as we could desire.

On KOBELLITE from OURAY, COL., and the CHEMICAL COMPOSITION of this SPECIES.

By Harry F. Keller.

[*Read at the Meeting of the Chemical Section, May 21, 1889.*]

The sulphobismutites and sulfostibnites of the southwestern part of Colorado, have repeatedly formed the subject of mineralogical and chemical research. Genth, Koenig, Hillebrand, and others have proved the occurrence there of a number of species already known from other localities, and have also described several new compounds of this class under the names of schirmerite, alaskaite and beegerite.

In the following pages, I desire to give the description of a mineral, possessing the composition $2(Pb,Ag_2,Cu_2)S.(Bi,Sb)_2S_3$ and to show further that it is in all probability identical with the kobellite of Setterberg.

The material for this investigation was kindly supplied by my brother, Mr. Hermann A. Keller, of Pueblo, Col. It consisted of several beautiful specimens of an ore that had been taken from the Silver Bell mine at Ouray, Col., by Mr. Philip Decker.

I have not been able to obtain any further information concerning the occurrence of the mineral, but consider it highly probable that it is closely analogous to that of alaskaite described by Koenig.* Like this it is found associated with barite and chalcopyrite. *Physical properties*:—Massive; structure, finely granular, inclining to fibrous; lustre, silky metallic; color, bluish lead-gray; fracture, uneven; streak, iron-black. Apparent hardness, 2·5—3; sp. gr., 6·334.

Chemical deportment.—Upon heating, the mineral first decrepitates violently and then fuses. In the open tube, it gives off sulphurous acid and a sublimate of antimonious acid. Upon charcoal it yields a yellow incrustation, with a white non-volatile fringe and a metallic globule, which for

* *Amer. Philos. Soc.*, June, 1881.

the greater part is volatilized upon continued blowing. The residue gives the reactions of iron and copper in the salt of phosphorus bead, and a button of metallic silver on cupellation. A crimson coating is obtained with potassium iodide and sulphur on charcoal.

Hydrochloric acid decomposes the compound with evolution of hydrogen sulphide, especially upon heating; the gangue material and chalcopyrite are left undissolved, while the silver passes into solution, from which it can be precipitated as chloride by diluting with water.

Chlorine, as well as nitric acid, exerts a powerful action upon it.

As the quantitative separation and estimation of the constituents present some difficulties, I will briefly indicate the course of an analysis which was found to be best adapted to this end. A portion of the mineral was treated with nitric acid. When proper care is taken, the oxidation is completed in an hour's time. The excess of the acid was then removed upon the water bath and the residue boiled with a solution of pure carbonate of soda. This treatment was continued until all the sulphuric acid, excepting the small quantity in the barite of the gangue, had passed in solution. The undissolved oxides and carbonates of the metals were then filtered off. The filtrate showed a bluish color, and was found to contain small quantities of copper, antimony and bismuth. These were precipitated, by hydrogen sulphide, after acidifying with hydrochloric acid, and the sulphur then determined in the filtrate as barium sulphate. This was purified after ignition, by heating with hydrochloric acid, then dissolving it in concentrated sulphuric acid and reprecipitating it finally with water.

The separation of the metals was effected as follows: The mixture of the oxides, carbonates, etc., was treated with nitric and tartaric acids, whereby only the gangue material ($BaSO_4$) remained undissolved. After the small quantity of sulphides before mentioned had likewise been taken up in the solution, the silver was precipitated as chloride in the cold; potassium hydrate was then added to the filtrate in excess and hydrogen sulphide passed into it. The

precipitate, consisting of the sulphides of all the metals except antimony, was filtered off, and the antimony determined in the liquid according to Bunsen's method as pentasulphide. The conversion of the pentasulphide into tetroxide served as a check, but gave invariably a slightly lower percentage.

The metallic sulphides were again oxidized with nitric acid, the latter removed by evaporation with sulphuric acid and the remaining sulphates treated with dilute sulphuric acid (1 : 8) in the cold. In this manner the lead is separated from the other metals, but not completely, as the insoluble sulphate always retains small quantities of bismuth. It is therefore dissolved in warm potash solution, which leaves the oxide of bismuth with some lead, and these can then be separated readily by a renewed treatment with nitric and sulphuric acids.

In the solution containing the sulphates of copper, bismuth, iron and zinc, the two first mentioned were precipitated as sulphides with hydrogen sulphide, filtered off, converted into the nitrates and separated from each other with ammonia and ammonium carbonate. Zinc and iron were finally separated and determined by the usual methods.

In order to ascertain which of the metals enter into the composition of the mineral, one portion of the substance (Analysis II) was dissolved in hydrochloric acid and the residue remaining analyzed separately.

Although chlorine acts strongly upon the finely divided powder, I did not succeed in effecting a complete decomposition by its means. All the samples analyzed were taken from different pieces of the ore.

ANALYSES.

	I.	*II.*	*III.*	*IV.*	*V.*	*Mean.*
S	18·37	—	18·46	18·33	18·39	18·39
Bi	27·97	28·51	28·68	28·46	—	28·40
Sb	7·19	7·25	7·91	7·84	—	7·55
Pb	36·11	36·08	36·25	36·20	—	36·16
Ag	3·22	3·39	3·30	3·32	—	3·31
Cu	2·43	2·26	2·91	2·76	—	2·59
Fe	1·31	1·35	1·69	1·65	—	1·50
Zn	·50	·37	·41	·31	—	·39
$BaSO_4$, etc., .	·43	·65	·21	·49	—	·45
	97·53		99·82	99·36		98·74

In No. II the portion insoluble in hydrochloric acid was found to contain (after the chloride of silver had been removed by ammonia):

Fe, 1·09. Cu, 1·12. Zn, ·24.

It seems therefore safe to assume* that the iron and an equivalent quantity of copper are present as chalcopyrite, and the zinc as sphalerite.

Now deducting these, plus the gangue and the loss, the percentage composition calculated from the mean results is as follows:

	Atomic ratio.		
S = 17·76	·5550	=	2·600
Bi = 30·61	·1457		
Sb = 8·13	·0677	·2134 =	1·000
Pb = 38·95	·1881		
Ag = 3·58	·0166	·2124 =	·995
Cu = ·97	·0077		
100·00			

and the formula is therefore: $2(Pb,Ag_2,Cu_2)S.(BiSb)_2S_3$. Since the atomic ratio of antimony† to bismuth is 1 : 2 the mineral may be considered as composed of one mol. of jamesonite with two mols. of cosalite.

The recent text-books of mineralogy do not assign this formula to any mineral, nevertheless such a one has been known for a long time.

As kobellite, Setterberg‡ in 1839 first described a mineral from the cobalt mines of Hvena, in Sweden, the composition§ of which he found to be:

S =	(18·61)
Bi =	28·37
Sb =	9·38
Pb =	40·74
Fe =	2·02
Cu =	·88
	100·00

* Chalcopyrite, when finely divided, is slightly acted upon by HCl.

† I have reason to believe that the antimony determinations I and II are a little too low.

‡ *Pogg. Ann.*, **55**, 536.

§ Recalculated with present atomic weights (Rammelsberg, *Mineraich.*, p. 100).

Deducting from this the copper with the equivalent quantities of iron and sulphur, the atomic ratios are as follows:

S	=	·5506		= 2·581
Bi	=	·1351	·2133	= 1·000
Sb	=	·0782		
Pb	=	·1966	·2187	= 1·025
Fe	=	·0221		

that is, they are identical with those calculated from my analyses.

Setterberg states distinctly that the iron of his mineral was dissolved in hydrochloric acid, and must therefore be considered as belonging to it; another slight difference in the composition of the minerals from the two localities is the replacement of about one-twelfth of the lead by silver in that from Ouray.

In 1862, Rammelsberg published an analysis of some material from the Hvena mine; he found:

S	=	18·22
Bi	=	18·60
Sb	=	9·46
As	=	2·56
Pb	=	44·25
Fe	=	3·81
Cu	=	1·27
Co	=	·68
		98·85

After deducting 5·61 per cent. of (FeCo)AsS and 3·67 per cent. of $CuFeS_2$, he arrives at the formula

$$Pb_3BiSbS_6.$$

In his *Mineralchemie* (p. 100), he gives an analysis of so-called kobellite from another locality (the name of which is not mentioned), and from this deduces the same formula.

He does not prove, however, that the analysis by Setterberg is incorrect, and it is more than likely that the material examined by him consisted of a mineral different from Setterberg's.

There are numerous instances of the occurrence of two different sulpho-salts of similar appearance in the same vein, and even upon the same piece.

The re-investigation of alaskaite by Koenig* was caused by it having been mistaken for cosalite from the same mine.

The specific gravity determinations also show a slight discrepancy; Setterberg found 6·29 — 6·32, while Rammelsberg's determination gave 6·145. That of the Ouray occurrence is 6·334.

In view of all these facts, I feel myself justified in retaining the name of kobellite for the mineral of the formula:

$$2(Pb,Ag_2,Cu_2,Fe)S.(Bi_{(2/3)}Sb_{(1/3)})S_3,$$

and would suggest that another name be given to that to which this name has hitherto been applied, namely,

$$Pb_3SbBiS_6.$$

In concluding, I desire to propose the name of lillianite for a mineral from the Lillian mine in Leadville, Col., described several years ago jointly by my brother and myself as a variety of kobellite. It possesses the composition $3(PbAg_2)S.Bi_2S_3$, and represents the bismuth mineral corresponding to boulangerite.

II.—ANALYSIS OF MEGABASITE FROM BONITA MOUNTAIN, NEAR SILVERTON, COL.

More than three years ago I received from Colorado, among other specimens, one which was labelled "gœthite." Some qualitative tests that were then performed upon it proved that it consists essentially of tungstic acid and manganous oxide. The occurrence has become quite well known since, but, as far as I am aware, no quantitative analysis of the material has been published. I may therefore be permitted to put the following on record:

Sp. Gr. = 6·780

WO_3	=	74·24
MnO	=	21·09
FeO	=	2·06
CuO	=	·11
MgO	=	trace
SiO_2	=	2·13
		99·63

CHEMICAL LABORATORY, UNIV. OF PA.,
PHILADELPHIA, May 21, 1889.

* *Proc. Amer. Philos. Soc.*, 1885, 211.

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM ZINC.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

[*Read at the Meeting of the Chemical Section, May 21, 1889.*]

The separation of these metals has been effected by Yver (*Bull. Soc. Chim. de Paris*, **34,** 18), who employed the acetates for this purpose.

Eliasberg (*Zeitschrift für Analyt. Chemie*, **24,** 548) and Smith and Knerr (*Am. Chem. Journal*, **8,** 210) confirmed this observation, at the same time emphasizing the fact that the current should be carefully regulated, otherwise unsatisfactory results would be obtained. A solution containing cadmium and zinc as tartrates, together with free tartaric acid, will also yield all its cadmium to a current generating 0·4—0·5 cc. oxy-hydrogen gas per minute (*Am. Chem. Journal*, **8,** 210). We have no record of other salts of these metals having been used for their electrolytic separation, and therefore have taken occasion to learn what the result might be with solutions of the double cyanides, such as we employed in separating mercury and copper (JOURNAL FRANKLIN INSTITUTE, **127,** 469, and *Am. Chem. Journal*, **11,** 264).

Beilstein and Jawein (*Ber. d. d. chem. Gesellschaft*, **12,** 446, 762) have shown that both cadmium and zinc can be completely precipitated from a cyanide solution, but have not given the current strength employed by them in their experiments, nor did they attempt the separation of these metals from each other.

As our experience with mercury and copper clearly indicates, it is frequently possible, by close attention to the current, to effect electrolytic separations, which ordinarily seem impossible. With this fact clearly before us, our first work with the metals now under consideration was to ascertain how feeble a current would suffice for the complete deposition of each metal, when alone in a cyanide solution, in the presence of an excess of an alkaline cyanide. We very soon discovered that the cadmium separated readily

and with a much weaker current than was necessary for the deposition of the zinc. The latter will, however, separate from a cyanide solution, even under the influence of a feeble current, but not until the excess of cyanide has been completely decomposed. With the quantity of cyanide used by us, and with a current of the strength indicated below, this complete decomposition of the alkaline cyanide is not likely to occur in a shorter period than forty-eight hours. Hence, it follows, that as the quantity of cadmium used in our experiments is entirely precipitated in a little more than eighteen hours, the complete separation of cadmium from zinc is thoroughly feasible by this method.

All our experiments were conducted in the cold, and care was taken in each case to examine the deposited metal for zinc, and the residual solution for cadmium. The conditions under which our work was carried on and the results obtained are these:

Metallic Cadmium in Grammes.	Cadmium found.	Metallic Zinc present.	Difference in per cent. of Cadmium.	KCN in Grammes.	Total Dilution.	Current in cc. of O-H Gas.	Time.
			Per Cent.				
·1817	·1813	. . .	− ·22	4·5 grammes in each separation.	200 cc.	0·3 cc. in each experiment.	18-23 hours.
	·1818	. . .	+ ·05				
	·1815	. . .	− ·11				
	·1822	. . .	+ ·22				
	·1812	·2000	− ·27				
	·1818	·2000	+ ·05				
	·1828	·2000	+ ·60				
·2426	·2422	. . .	− ·16				
	·2432	. . .	+ ·24				
	·2426	. . .	. . .				
	·2420	·2000	− ·24				
	·2435	·2000	+ ·30				
	·2429	·2000	+ ·12				
	·2426	·2000	. . .				
	·2433	·2000	+ ·28				
	·2434	·2000	+ ·32				

The cadmium deposit was light gray in color and crystalline in structure. It was washed with hot water and dried upon a warm iron plate.

CHEMICAL LABORATORY OF THE UNIV. OF PA.,
PHILADELPHIA, May 21, 1889.

DERIVATIVES OBTAINED FROM MONOCHLORDINITROPHENOL AND BASES OF THE AROMATIC SERIES.

By Edgar F. Smith.

[*Read at the Stated Meeting of the Chemical Section, May 21, 1889.*]

It is well known that picric acid combines readily with bases and the higher hydrocarbons of the aromatic series to form well crystallized and stable compounds. It has, however, not been observed that phenols, containing less than three nitro-groups, together with other negative groups or elements, possessed this acidic property of picric acid. Several years ago (*Am. Chem. Journal*, **1**, 180) I discovered that when monochlordinitrophenol (1 : 2 : 4 : 6) and aniline were brought together there resulted a rather stable derivative, which did not decompose in aqueous solution until after prolonged boiling. Recently I have obtained derivatives with this same chlordinitrophenol and the bases and hydrocarbon mentioned below.

The phenol itself forms yellow-colored needles, melting at 80° C. Its *α-naphthylamine* derivative consists of brownish-yellow crystalline tufts, composed of velvety needles, melting at 131° C., and solidifying at 110° C. It was obtained by dissolving equal quantities of the phenol and *α*-naphthylamine in hot alcohol; on cooling, the new compound separated quite rapidly. It dissolves in warm water. The *o-toluidine* derivative, obtained by heating together equivalent quantities of the phenol and toluidine, consists of golden yellow plates, soluble in hot alcohol. It melts at 140° C., and solidifies at 115° C.

The *p-toluidine* compound separated from its alcoholic solution in reddish-yellow needles, was quite soluble in water, and melted at 157° C. With *urea* the phenol does combine, but the union is evidently unstable, since by exposure to the air a gradual change in color was perceptible. The *carbazol* compound consists of intensely red colored needles, melting at 121° C. It dissolves quite readily in alcohol.

With *p-nitraniline* long needles were obtained. Their color resembled that of chromic acid. It was rather difficult to obtain them pure. The *anthracene* derivative forms plates with an intense red color. The union is not stable, and exposure to the air causes a gradual decomposition. The *morphine* compound is made up of bundles of needles, having a deep vermilion color. It dissolves in alcohol, and melts at 97° C. The combination with *propylamine* is a yellow, crystalline solid; that with *strychnine* consists of yellow nodular crystals, melting at 212° C.

The determination of the carbon and hydrogen in the aniline compound, and that of the nitrogen in the *α*-napthylamine and *o*-toluidine derivatives, show that all the products described above are very probably combinations of a molecule of the chlordinitrophenol, with a like amount of the basic body.

I have further observed that dichlormononitrophenol, obtained in the nitration of dichlorsalicylic acid (*Am. Chem. Journal*, **8**, 98), does not unite with aniline, so that it would seem that the acidic character of the phenol reached its limit with the dinitro-product; and that union with bases such as those given above, is not possible when but one NO_2 group is present.

The facts here communicated are to be regarded as preliminary to an investigation now going on, but which must shortly be suspended for some months.

Chemical Laboratory of Univ. of Pa.,
Philadelphia, May 21, 1889.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, September 17, 1889.*]

HALL OF THE FRANKLIN INSTITUTE.
PHILADELPHIA, September 17, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: W. H. Bower, Reuben Haines, H. W. Jayne, L. J. Matos, W. W. McFarlane, Thos. N. Newbold, H. Pemberton, Jr., Dr. Wm. H. Wahl, W. D. Weikel.

The resignation of Marshall R. Pugh, to take effect at the end of current year, was presented and accepted. The President read a copy of a proposed amendment to the By-Laws of the INSTITUTE relating to Sections, under which the Sections would be empowered to admit to associate and corresponding membership others than members of the INSTITUTE.

The President exhibited several specimens of the aqueous solution of the allotropic silver, described by Mr. M. Carey Lea.

Dr. Wahl presented for inspection a specimen of aluminium, manufactured at present on the commercial scale by the Pittsburgh Reduction Company. The process employed is that of —— Hall, of Oberlin, O., which consists substantially in dissolving alumina by igneous fusion in a bath of metallic fluorides, and electrolyzing the resulting solution, by which, it is affirmed, the alumina is decomposed while the solvent remains unaffected. Dr. Wahl spoke in general terms of certain technical applications of aluminium, especially to the increasing use of ferro-aluminium by foundrymen to improve inferior irons. He also exhibited several medallions struck from aluminium, made by the Aluminium Company, limited, at the works at Oldbury, near Birmingham, England. They had been presented by Mr. H. Y. Castner, whose process is there in operation.

Adjourned. H. W. JAYNE, *Secretary pro tem.*

Following is a list of the members of the CHEMICAL SECTION at the present time:

Allen, A. W.,	Pencoyd Iron Works, Pencoyd, Pa.
Bower, Henry,	Twenty-eighth and Gray's Ferry Road.

Bower, W. H.,	Twenty-eighth and Gray's Ferry Road.
Browning, G. G.	44 N. Front St.
Bullock, Charles,	528 Arch St.
Bullock, Wm. W.,	528 Arch St.
Campbell, J. H.,	Kingman, Mojave Co., Ariz.
Carter, John E.,	Coulter and Knox Sts., Germantown.
Chase, Prof. R. L.,	1336 Spring Garden St.
Clarkson, Philip S.,	Quaker City Dye Works, 110 Oxford St.
Cresson, Dr. Chas. M.,	413 Locust St.
Day, Prof. W. C ,	Swarthmore College.
DeBalas, Victor,	44 N. Front St.
Eastwick, J. H.,	Wissahickon Station.
Eastwick, A. T.,	Wissahickon Station.
Fisher, R. A.,	2239 St. Alban's Place.
Frankel, Lee K.,	University of Pennsylvania.
Frazer, Dr. Persifor,	Drexel Building, Room 1042.
Garrison, F. Lynwood,	Radnor, Pa.
Greene, Dr. Wm. H.,	204 N. Thirty-sixth St.
Haines, Reuben,	738 Sansom St.
Hall, Prof. L. B.,	Haverford College.
Hooker, Dr. S. C.,	Franklin Sugar Refinery.
Hunter, Thos. G ,	Fifty-fifth St. and Paschall Ave.
Ives, Fred. E ,	Crosscup & West, Ninth and Filbert Sts.
Jayne, E. C.,	242 Chestnut St.
Jayne, H. W.,	931 N. Broad St.
Keiser, Dr. E. H.,	Bryn Mawr College.
Keller, Dr. H. H.,	University of Pennsylvania.
Koenig, Dr. Geo. A.,	University of Pennsylvania.
Lea, M. Carey,	430 Walnut St.
Lewin, F. C.,	1011 Spruce St.
Lewis, John T.,	242 S. Thirteenth St.
Lichenheim, Jacob,	1614 N. Tenth St.
Lüthy, Otto,	2336 Fairmount Ave.
McFarlane, W. W.,	1600 Park Ave.
Matos, L. J.,	3943 Fairmount Ave.
Morris, Dr. L. I ,	2505 Oxford St.
Morton, Prof. Henry,	Stevens Institute of Technology, Hoboken, N. J.
Mucklé, Dr. Alex.,	1323 N. Nineteenth St.
Newbold, Thos. N.,	608 S. Forty-second St.
Newhall, Geo. M.,	136 S. Fourth St.
Oatley, Dr. E. L.,	4003 Chestnut St.
Palmer, T. C.,	22 N. Front St.
Pemberton, H.,	1947 Locust St.
Pemberton, H., Jr.,	1947 Locust St.
Petraeus, C. V.,	231 S. Front St.
Phillips, Geo. B.,	622 Race St.

Rand, Theo. D.,	17 S. Third St.
Rittenhouse, H. N.,	218 N. Twenty-second St.
Rowland, W. L.,	4800 Chester Ave.
Sadtler, Prof. S. P.,	204 N. Thirty-fourth St.
Schaffer, Dr. Chas.,	1309 Arch St.
Semper, C. J.,	505 S. Forty-first St.
Shaw, H. G.,	Thirty-second and Gray's Ferry Road, care Kalion Chemical Co.
Smith, Prof. Edgar F.,	University of Pennsylvania.
Thomas, Prof. N. Wiley,	Girard College.
Trimble, Prof. H.,	632 Marshall St.
Tuttle, Dr. N. K.,	U. S. Mint.
Wahl, Dr. Wm. H.,	Franklin Institute.
Warden, Henry,	307 Walnut St., 18th St. and Allegheny Ave.
Webster, Geo. C.,	Media, Pa.
Weikel, W. D.,	Merchantville, Camden Co., N. J.
Whitney, Asa W.,	1815 Vine St.
Wiegand, S. Lloyd,	146 S. Sixth St.
Wolf, Dr. T. R.,	Newark, Del.
Wolff, Lawrence, M.D.,	333 S. Twelfth St.
Wyeth, F. H.,	1412 Walnut St.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, October 15, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, October 15, 1889.

MR. T. C. PALMER, Vice-President, in the Chair.

Members present: Dr. L. B. Hall, Dr. Wm. H. Wahl, Prof. N. Wiley Thomas, Mr. W. W. McFarlane, Mr. C. J. Semper, Mr. Lee K. Frankel, Mr. Reuben Haines, Mr. A. Weikel, Mr. J. H. Eastwick, Mr. F. C. Lewin and a number of visitors.

The following gentlemen were nominated for membership in the Section: Mr. Geo. L. Norris, Pencoyd, Pa.; Mr. Hugh A. Galt, 1011 Spruce Street, Philadelphia; Mr. Lucius E. Williams, Swarthmore College, Swarthmore, Pa.; Mr. Hermann Schanche, Gray's Ferry Chemical Works, Philadelphia.

Dr. Wahl made some remarks on the industrial production of aluminium by electrolysis, supplementing his comments of last meeting. He referred to the process of M. Adolphe Minet, in operation industrially at Creil (Oise), France, and which in essential parts was identical with that of Mr. Hall. Mr. Minet electrolyzes a bath composed of forty per cent. of cryolite and sixty per cent. of chloride of sodium, maintained in the state of igneous fusion. The bath is continually regenerated by additions of alumina (or bauxite). The interesting point in considering the two processes, the speaker stated, was the different explanations of the operations taking place in the bath under the action of the electric current upon substantially the same components; Hall claiming that the alumina undergoes electrolysis, the solvent fluorides being unaffected, and Minet that the fluorides are electrolyzed, the liberated fluorine acting upon the alumina, to form fresh fluoride, thus maintaining the bath. The explanation of M. Minet, the speaker held, to be the rational one. Adjourned.

WM. C. DAY, *Secretary.*

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, November 19, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 19, 1889.

MR. T. C. PALMER, Vice-President, in the Chair.

Members present: Prof. R. L. Chase, Mr. A. T. Eastwick, Mr. Lee K. Frankel, Mr. F. Lynwood Garrison, Mr. Reuben Haines, Prof. L. B. Hall, Dr. H. W. Jayne, Dr. H. H. Keller, Mr. F. C. Lewin, Mr. Otto Lüthy, Mr. W. W. McFarlane, Mr. W. L. Rowland, Prof. S. P. Sadtler, Prof. Edgar F. Smith, Prof. N. Wiley Thomas, Dr. Wm. H. Wahl, Mr. L. E. Williams and two visitors.

The following gentlemen were elected to membership in the Section: Mr. Geo. L. Norris, Pencoyd, Pa.; Mr. Hugh A. Galt, 1011 Spruce Street, Philadelphia; Mr. Lucius E. Williams, Swarthmore College, Swarthmore, Pa.; Mr. Hermann Schanche, Gray's Ferry Chemical Works, Philadelphia.

Dr. Jayne asked for information on By-Law IV regarding the dropping of delinquent members. The question was as to the necessity of action on the part of the Section in such cases. It was decided that no special action of the Section was necessary, but that delinquent members shall, at the proper time, simply be dropped from the list; in accordance with this decision, the Treasurer notified the Secretary to drop the names of two delinquents from the list.

The nomination of officers for the ensuing year was then taken up. The following nominations for President were made: Mr. T. C. Palmer, Prof. S. P. Sadtler, Prof. R. L. Chase. On motion, the nominations for President were closed.

Nominations for two Vice-Presidents were then made. The following gentlemen were put in nomination: Dr. H. H. Keller, Mr. W. L. Rowland and Prof. Henry Trimble. On motion, the nominations for Vice-Presidents were closed.

Dr. W. C. Day was nominated for Secretary, Dr. H. W. Jayne for Treasurer, and Dr. Wm. H. Wahl for Conservator.

Mr. W. W. McFarlane gave a description of some new dyeing materials, in which he explained the use of a number of dyes which have recently been introduced into this country by the representatives of Fried. Bayer & Co., of Elberfeld; samples of dyed products were also exhibited.

Among other interesting matters, the speaker stated that "carmine blue" is dyed with the use of Glauber's salt and sulphuric acid, in the same way as indigo carmine or extract, and further, that the carmine blue will probably displace the indigo extract at no distant period in the future. "Sulphon Azurin" is also used in dyeing cotton, using a boiling bath and some alkaline salt, such as borax, sal-soda, sodium phosphate or silicate. The blue produced is similar in shade to that of indigo, and is said to withstand the action of light and of dilute acids as well.

Benzo-black-blue is dyed in cotton in the same way as other benzo colors, and very dark shades are the result. There are two shades of this color, designated respectively as G and R.

The paper was discussed by Messrs. McFarlane and Palmer. Dr. Wahl, from whom a paper was expected, announced that he must defer, until a later meeting, his paper on "a new gold-like alloy;" and gave in place of this, a statement of further results obtained by him in the electrolytic deposition of platinum, exhibiting specimens of work. As the investigation is not yet entirely completed, and certain details of the mode of procedure are to be made the subject of letters-patent, the speaker preferred, for the present, to withhold the same from publication. Dr. Wahl also made some critical remarks on statements made in a paper by A. J. Rogers, on "Experimental Researches in the Reduction of the difficultly-reducible Metals," which was published in the *Proceedings of the Wisconsin Natural History Society*, April, 1889, expressing doubts, based on theoretical considerations, as to the accuracy of one of the results announced by the author; namely, that he had obtained "a yield of aluminium six times greater than had ever been obtained by electrolysis."

Mr. F. Lynwood Garrison presented some remarks on the Paris Exposition, with special reference to Metallurgy and Fuels. As these remarks will be embodied later on in a full and comprehensive report to the INSTITUTE, they are omitted here; this paper was followed by a general discussion of some of the statements it included.

Prof. E. F. Smith read a paper on the occurrence of vanadium in caustic potash. This paper was referred for publication. He then presented another on the subject of nitration by the use of nitrogen trioxide as obtained by the action of nitric acid on arsenic trioxide. This paper was also referred for publication.

Professor Smith next presented the following results of further work in the electrolysis of metallic sulphocyanide solutions. His object in presenting these results was to reserve for the future the field upon which he has entered. In addition to the results already reported in a former paper, it was observed that iron, cobalt and nickel in sulphocyanide solutions were fully deposited

by weak currents, and that the presence of a sulphocyanide in manganese solutions prevented the formation of the dioxide, and when the latter had already precipitated the addition of KCNS would effect its re-solution. To these facts may be added that mercury, cadmium, bismuth and lead deposit from sulphocyanide solutions. With lead, a behavior analogous to that noted with manganese was observed.

Approximate quantitative separations were made in several cases, but the complete development of these observations requires further study. Another line of experiment has been the electrolysis of metallic phosphates in the presence of free phosphoric acid. Mercury, silver, copper, cadmium, lead, iron, zinc, cobalt, and manganese have given interesting results qualitatively, and quantitatively. Separations seem possible when regard is had to the proper condition of the current. The speaker stated that although in possession of quantitative figures in some of these cases, he preferred to postpone their publication until a careful examination has been made with each metal. Curiously enough, with manganese phosphate dissolved in phosphoric acid there is no separation of dioxide; the solution slowly acquires a red tint, and in time becomes turbid, although the addition of more acid causes the turbidity to disappear.

Dr. Warwick, at the request of Professor Smith, has begun an electrolytic study of the metallic formates; the results obtained will be communicated later.

Adjourned.

WM. C. DAY, *Secretary.*

EXPERIMENTAL RESEARCHES IN THE REDUCTION OF THE DIFFICULTLY-REDUCIBLE METALS.

By A. J. Rogers.

[*Reprinted from the Proceedings of the Wisconsin Natural History Society, April, 1889.*]

This pamphlet of eighteen pages gives the result of experiments made by the author, upon the reduction of sodium and of aluminium from their salts, by electrolysis, at a high heat. The experiments are carefully made, giving proportions of raw materials, strength of current, time employed, and practical results as compared with the theoretical. The author gives first a *résumé* of some conclusions arrived at in a paper by him, read before the American Association for Advancement of Science, at Ann Arbor, in 1885, in which among other points established, he finds that from fused sodium chloride, 61 per cent. of the theoretical amount of sodium is reduced by electrolysis; this being the average result of six experiments. It thus seems that with suitable apparatus from 5 to 6 pounds of Na could be produced in 24 hours to one electrical horse-power, thus, if there were no practical difficulties in the construction of crucibles and other apparatus involved, nor in working continuously on a large scale with a raw material so cheap and pure as NaCl, the metal could be obtained at a small cost and could be applied to the reduction of other difficultly-reducible metals, including that very valuable metal Al.

He next turns his attention to the alloys of sodium with lead, and also with tin. He finds that "they can be heated to a higher temperature than pure Na or K, in acid (silicious) crucibles, without the Na or K attacking the crucible."

Description of the properties of the sodium-lead alloys are given: the proportions of the two metals varying from 1 part of sodium with 9 parts of lead, up to 1 part sodium with $1\frac{5}{6}$ parts lead. These richer alloys can be cut with a knife, like sodium, and act very rapidly when thrown upon

water. The same properties are peculiar to the sodium-tin alloys.

These alloys are formed by passing a current through melted NaCl in crucibles containing lead or tin serving as a cathode.

A series of nine experiments are reported, in most of which, however, cryolite was mixed with the salt. A small amount of aluminium was in all cases reduced, which was separate mostly from the lead- or tin-sodium alloy. But the principal yield of Al was obtained by heating the sodium alloy with cryolite afterwards in another crucible. It may be interesting to cite a part of one experiment.

"*Experiment 8.*—Passed 80 ampères with 24 volts through four crucibles in series, for six hours, using 1 part of cryolite to 3 parts of NaCl with 450 grains lead in each crucible. * * * Two hundred and fifty grains of quite pure Al was obtained, with a large amount of Na in the remelting with cryolite. There was then actually obtained, besides all losses, in round numbers, 1 pound of Al to the electrical horse-power per day of 24 hours.

"Probably 8 to 10 per cent. can be obtained from cryolite, where the theoretical yield is 12·85 per cent.

"The best results, and, in fact, the only quantitative results that have yet been published, so far as I am aware, for the separation of Al by electrolysis, are reported by Dr. John Hopkinson, of the Kleiner process, where 3 grains were produced to the electrical horse-power per hour, which would be about one-sixth of a pound in 24 hours."

Mr. Rogers' results may be summed up as follows:

(1) The formation of a rich alloy of lead or tin with sodium, by electrolyzing common salt at a high heat, in presence of lead or tin.

(2) The reduction of aluminium from cryolite, or from the double chloride of aluminium and sodium, by simple heating with the above sodium alloy.

(3) A yield of aluminium, six times greater than has ever been obtained by electrolysis.

His paper is well worth the attention of all metallurgists.

P.

ACTION OF THE GAS FROM As_2O_3 AND HNO_3 UPON *p*-OXYBENZOIC ACID.

By Edgar F. Smith.

[*Read at the Stated Meeting of the Chemical Section, November 19, 1889.*]

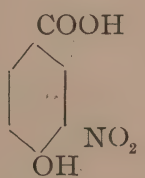
In vol. viii, p. 99, of the *American Chemical Journal*, I called attention to the fact that when methyl salicylate, in ethereal solution, was exposed to the gas arising from arsenic trioxide and nitric acid, ethers of α and β-meta-nitro-salicylic acids were produced. This procedure gave a ready method for the production, as well as an easy means of separating these two acids, the ether of the α-acid being readily soluble, while that of the β-acid was practically insoluble in ether.

The ethyl ether of meta-oxybenzoic acid, in ether, gave when acted upon as above ethers of β-nitro-meta-oxybenzoic acid (m. p. 230° C.) and trinitro-meta-oxybenzoic acid (m. p. 111° C.). The details of this investigation may be found in the *Proceedings of the American Phil. Soc.*, September 7, 1888. I have recently experimented in the same line wih *p*-oxybenzoic acid. The starting point was ethyl para-oxybenzoate, prepared according to the recommendation of Hartmann in the *Journal für praktische Chemie* [II], **16,** 50. The ether thus obtained, after crystallization from water, gave the constant melting point 112°·5 C., as stated by Graebe (*Annalen*, **139,** 146), and not 116° C., as given by Hartmann. The pure ether was next dissolved in ordinary ether, and the solution then acted upon for one and one-half hours, in the cold, by the vapors from nitric acid and arsenic trioxide. The flask containing the ethereal solution was corked and allowed to stand in a cool place for several days, after which the ether was distilled off. The residue was dark and oily, but after several hours became solid and crystalline. By solution in hot alcohol and recrystallization long, stout, red-colored needles were obtained. These melted regularly at 69°–70° C. Barth (*Journal für prakt. Chemie*,

100, 369), speaking of the action of nitric acid upon ethyl *p*-oxybenzoate mentions two products, ethyl nitroparaoxybenzoate and ethyl dinitroparaoxybenzoate. His description of the mononitro-ether is so meagre that I was not able to determine at first whether I was dealing with a well-known compound or an entirely new product. The subsequent analysis of the free acid left no doubt as to the identity of my compound and that described by Barth. This chemist remarks that the melting point of the nitro-ether lies below —100° C., I have found it as above —69°–70° C. On boiling the ether with caustic potash for some time and then acidulating the alkaline liquid a crystalline mass separates. It dissolves readily in hot water, crystallizing from it, on cooling, in long needles with a faint yellow color. At times the needles showed a flesh-red color; this was removed by boiling the aqueous solution with animal charcoal. When pure the acid melted at 184°–185° C., the same as the acid obtained by Barth. A nitrogen determination, made by Mr. Seal of this laboratory, gave 7·95 per cent. N. The required N for a mononitro-*p*-oxybenzoic acid is 7·65 per cent.

An attempt to estimate the nitrogen in the ether by the Kjeldahl method, failed.

Griess (*Berichte*, **20**, 480) also obtained nitro-*p*-oxybenzoic acid of melting point 185° C., and showed that it was identical with the acid he had previously prepared from *p*-amidonitro-benzoic acid by boiling with KOH, so that its constitution and that of the acid prepared by me as above described is undoubtedly



Hasse (*Berichte*, **10**, 2,188) states that nitro-*p*-oxybenzoic acid contains water of crystallization. The acids of Barth, Griess and myself are anhydrous.

While *p*-nitro-oxybenzoic acid requires a large volume of

hot water for its solution, its sodium salt is very soluble, and from its concentrated liquid separates in beautiful red colored needles forming bundles.

The amide of the acid (C_6H_3 (NO_2) OH. $CONH_2$) consists of beautiful orange-yellow colored tufts. It melts at 160°–161°, and dissolves easily in hot alchohol.

The above account concludes my study of the action of the vapors from nitric acid and arsenic-trioxide upon the three hydroxy-benzoic acids. The results briefly summarized are these:

With ortho-oxy-benzoic acid two nitro acids were obtained; with meta-oxy-benzoic acid one nitro acid and a tri-nitro-meta product resulted, and with para-oxy-benzoic acid one meta-nitro acid.

The course of the reaction in these three cases (the *m*-oxy-acid excepted) was not attended by any troublesome intermediate products, and for this reason the method may perhaps become serviceable in the nitration of other oxy-acids.

Chemical Laboratory of the Univ. of Pa.,
Philadelphia, November 18, 1889.

VANADIUM IN CAUSTIC POTASH.

By Edgar F. Smith.

[*Read at the Stated Meeting of the Chemical Section, November 19, 1889.*]

The occurrence of vanadium in commercial caustic soda has been noticed (See Baumgarten, *Zeitschrift für Chemie*, 1865, **605,** and Donath, *Zeitschrift für Analyt. Chemie*, **21,** 45). As far as I am aware, it has not been observed in caustic potash, hence the following lines.

While engaged in making certain decompositions, for which I employed the ordinary stick potash, I was rather surprised, after saturating the alkaline solutions with hydrogen sulphide, acidulating with hydrochloric acid, and heating for several hours, to discover that the separated sulphur showed a decidedly chocolate-brown color. This occurred repeatedly. The quantity of dark material was never very great, yet it was present, even in potash from alcohol. Some preliminary experiments were made which pointed to vanadium. I therefore saturated the warm aqueous solution of three pounds of stick potash with hydrogen sulphide. Heat was applied for several hours longer, and during this period the liquid gradually assumed a yellow to deep red color. Hydrochloric acid was added to distinct acid reaction. The separated sulphur was quite dark in color. After filtration and washing, the residue was dried and treated with carbon disulphide to extract the free sulphur. The chocolate-colored mass remaining after this treatment dissolved, with exception of a slight quantity, in yellow ammonium sulphide, from which it was reprecipitated by dilute acid. Again washed, treated with carbon disulphide, and carefully ignited, there remained a crystalline mass. With a small quantity of this last product I made the phosphorous bead test—yellow, passing through dark to green when cool. Another special test consisted in dissolving a portion

of the ignited residue in a drop of conc. sulphuric acid, free from iron. One cc. of water was next added, and to this colorless solution from one to three drops of a dilute potassium ferrocyanide solution, whereupon the liquid acquired a fine green coloration. This latter test Dr. Walz (*American Chemist*, vol. vi, p. 453) employed in detecting the minute quantities of vanadium in American magnetites. He considers it conclusive evidence of the presence of vanadium. The most important test, and that which I applied to the remainder of the ignited residue, after effecting its solution in nitric acid, was to add a large piece of ammonium chloride to the ammoniacal solution. The morning following, crystals of ammonium vanadate had separated. These gave the true vanadium bead, and when ignited, moistened with pure, strong nitric acid and evaporated, left the deep red-colored residue characteristic of vanadium compounds.

The vanadium sulphide, as first obtained, was impure, consequently the reactions were at times masked, and it was only after eliminating some silver and iron that the reactions were unquestionable.

The impure sulphide from the three pounds of caustic potash weighed about one-half gramme.

CHEMICAL LABORATORY OF THE UNIV. OF PA.,
PHILADELPHIA, November 18, 1889.

PROCEEDINGS.

[*Stated Meeting, held at the* INSTITUTE, *Tuesday, December 17, 1889.*]

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, December 17, 1889.

Mr. H. PEMBERTON, Jr., President, in the Chair.

Members present: Prof. E. F. Smith, Dr. L. B. Hall, Dr. H. W. Jayne, Dr. S. C. Hooker, Prof. N. Wiley Thomas, Mr. J. H. Eastwick, Mr. L. J. Matos, Mr. W. H. Bower, Mr. T. C. Palmer, Mr. Lucius E. Williams, Dr. D. K. Tuttle, Mr. G. L. Norris, Mr. F. C. Lewin, Dr. W. C. Day and a number of visitors.

An extract from a letter of Dr. Wahl to the Secretary was read, recommending the renewal of subscriptions to the various journals taken by the Section. On motion, it was decided to authorize Dr. Wahl to renew these subscriptions.

The Treasurer, Dr. Jayne, read his annual report, showing the present financial condition of the treasury. The report showed a total of receipts from various sources amounting to $181.35; disbursements amounting to $89.85; thus leaving a cash balance of $91.50 in the hands of the Treasurer at date. The number of members on the books January 1, 1889, was 55; of these 5 were dropped for non-payment of dues, 3 resigned; during 1889 24 new members were added to the list, making a total of 71 now on the roll.

The election of officers for the coming year was then proceeded with, Prof. N. Wiley Thomas and Mr. W. H. Bower being appointed by the President to serve as tellers. Balloting for President and two Vice Presidents resulted in the election of Mr. T. C. Palmer, President, and Dr. H. F. Keller and Mr. W. L. Rowland, Vice-Presidents.

On motion of Dr. Hall, it was decided that the Secretary cast the vote of the Section for the present incumbents of the offices of Secretary, Treasurer and Conservator.

Dr. S. C. Hooker called the attention of the Section to a note by Dr. Samuel Rideal in the *Chemical News*, of November 29, 1889, in which the author gave the quantitative results of a comparison of the so-called "phenol-

sulphuric acid" method and the "carbazol" method of determining nitrates in potable waters; the figures are as follows:

NITROGEN IN PARTS PER 100,000.

Sample.	*Phenol-Sulphuric Acid.*	*Dr. Hooker's Carbazol Process.*
1	0·025	0 0247
2	0·050	0·045
3	0·200	0·209
4	1·400	1·38
5	1·600	1·65

Dr. Hooker then spoke of some experiments which he had made with Mr. Geo. Bartram during the past summer, showing that the phenol-sulphuric-acid solution used in the well-known process above referred to, undergoes a change shortly after preparation, which causes the introduction of a very appreciable error in the presence of comparatively large quantities of chlorides. When the phenol solution is freshly prepared, chlorides do not influence the results. These experiments will be published in detail at a later date.

Prof. E. F. Smith read a paper giving additional results obtained by himself and Mr. Lee K. Frankel in making electrolytic separations of various metals. The paper was submitted for publication.

Mr. G. L. Norris then read a paper on "A Rapid Method for Determining Phosphorus in Iron and Steel," modified from a method proposed by Dr. Drown, at the meeting of the American Institute of Mining Engineers, June, 1889. This paper was also referred for publication.

Adjourned.

Wm. C. Day, *Secretary.*

A RAPID METHOD FOR PHOSPHORUS IN IRON AND STEEL, MODIFIED FROM A METHOD PROPOSED BY DR. THOS. M. DROWN.

By G. L. NORRIS, Pencoyd, Pa.

[*Read at the Stated Meeting of the Chemical Section, December 17, 1889.*]

The new method for phosphorus described in Dr. Drown's paper before the Am. Inst. Min. Eng., June, 1889, and published in the *Technology Quarterly* for April, appeared to possess so much advantage over the Emmerton method in speed, that I determined to experiment with it, with the view of adopting it. My experiments convinced me that the 1·135 sp. gr. nitric acid, recommended by Dr. Drown, is superior to 1·20 sp. gr. nitric acid for dissolving pig-iron and steel for phosphorus determinations. I also found that the addition of ammonia or the presence of ammonium nitrate was of no advantage.

Finally I adopted the following modified method, doing away entirely with the use of ammonia:

Five grams of pig-iron or steel are treated in a twelve-ounce covered beaker, with 90 cc. of 1·135 sp. gr. nitric acid for steels, 120 cc. for pig-irons. The beaker is heated on an iron plate until all action ceases and solution begins to boil. To the boiling solution 20 cc. of a solution of potassium permanganate, eight grams to the liter, are added. The solution is then boiled a few minutes, to be sure all the permanganate is used up. A precipitate of manganese peroxide must come down on boiling to be sure that all the phosphorus is oxidized. After boiling with permanganate, a small piece of tartaric acid is added, and the solution boiled a minute or two longer, until all the manganese peroxide is dissolved. The solution is then poured in a 500 cc. globe flask and 10 cc. of 1·40 sp. gr. nitric acid added. The solution in the flask should then be about 90 cc. in bulk. In

case of pig-iron the solution is made up to 100 cc. with water, the graphite filtered off, and 80 cc. of the filtrate drawn off into a flask, and then 10 cc. of 1·40 sp. gr. nitric acid added. The solution is then heated to 90° C., and 80 cc. of ammonium molybdate solution added, the flask stoppered, wrapped in a cloth and shaken hard for five minutes. The molybdate solution is made by dissolving 100 grams molybdic acid in 400 cc. strong ammonia and then mixing with 1,200 cc. of 1·20 sp. gr. nitric acid. From this point on the method is the same as Emmerton's, reduction of the yellow precipitate with zinc and titration with a standardized permanganate of potassium solution.

For high phosphorus pig-iron only 1·25 grams are used and treated with 60 cc. of 1·135 sp. gr. nitric acid. The solution is made up to 100 cc., filtered, 80 cc. of the filtrate drawn off, and 10 cc. of 1·40 sp. gr. nitric acid added.

The only speed determination I have made was on a steel, and thirty-six minutes covered everything, weighing and all. The following analyses are all the check analyses I have made by this method.

	Emmerton Method.	New Method.
Open hearth steel,	·087	·086
		·087
		·085
		·087
		·086
		·088
		·086
		·087
		·087
		·086
		·087
		·087
		·088
Open hearth steel,	·051	·050
		·050
		·049
		·052
		·050
		·052
		·049
		·051
		·050
Open hearth steel,	·060	·062
		·061
		·060
Open hearth steel,	·063	·060
		·062
		·061
		·061
		·060
		·063
		·063
		·063
Crucible steel,	·076	·077
		·076
		·076
		·078
		·076
		·075
		·076
		·078
		·076
		·076
		·075
Bessemer steel,	·109	·109
		·109
		·108
		·109
		·110
		·107
		·109
		·110
		·109
Bessemer steel,	·105	·103
		·102
Clapp-Griffiths steel,	·273	·272
		·271
		·268
Bessemer pig-iron,	·023	·022
		·022
		·020
Bessemer pig-iron,	·094	·095
		·093
		·094
		·093
Bessemer pig-iron,	·043	·043
		·041
		·044
		·043
		·041
		·043
		·043
		·043
		·043
		·044
		·041
Swedes pig-iron,	·876	·874
		·873
		·875
		·877

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